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Chemically Active Fluid Bed for SOx Control
Volume III. Sorbent Disposal

Westinghouse Research and Development Center
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16. ABSTRACT: The report describes a laboratory investigation of three areas of the chemically active fluidized-bed (CAFB) process: residue characterization, leaching property, and thermal activity. Results indicate that further processing is required to meet environmental constraints. The environmental impact of CAFB residue disposal is also compared with results of conventional residues (flue gas desulfurization and lignite ash) from parallel tests. The impact of the recently enacted Resource Conservation and Recovery Act is assessed. The CAFB process was developed to convert high-sulfur heavy oils and low-grade coal to clean, medium heating value fuel gas in conventional boilers. Disposal of the spent sorbent, which consists of varying amounts of CaO, CaS, and CaSO4, may cause environmental concerns associated with potential air, water, odor, and heat pollution. The spent sorbent can be further processed to reduce its environmental impact by methods including dry sulfation, dead-burning, room-temperature fly-ash blending, high-temperature processing, and slurry carbonation.

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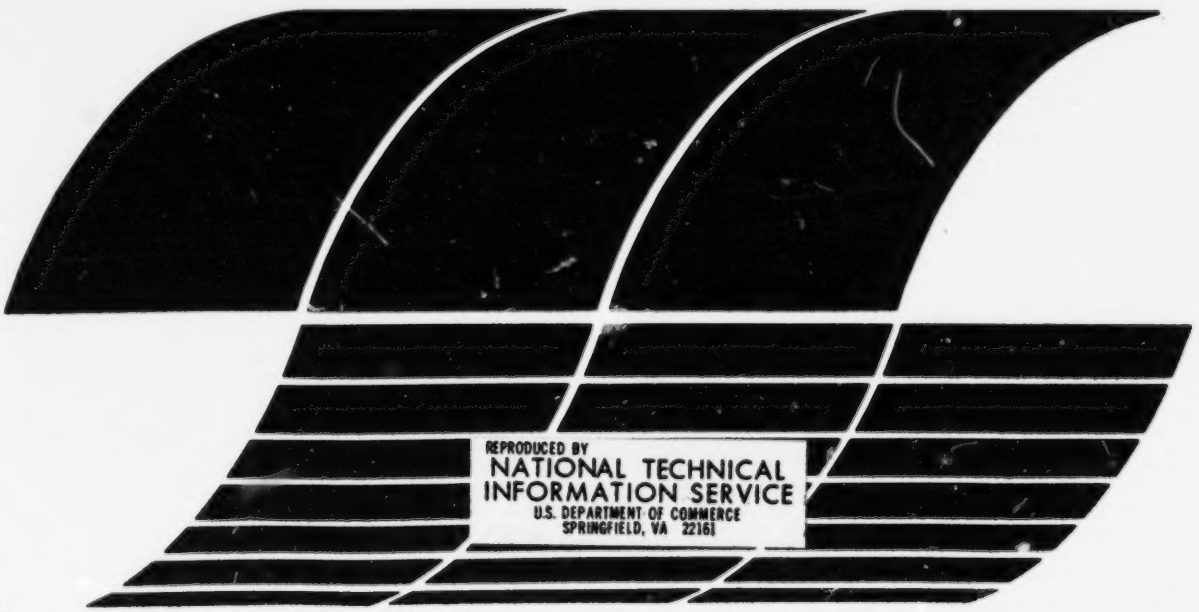

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July 1979

Chemically Active Fluid Bed for SO_x Control: Volume 3. Sorbent Disposal

by

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PREFACE

The Westinghouse Research and Development Center is carrying out a program under contract to the United States Environmental Protection Agency (EPA) to provide experimental and engineering support for the development of the Chemically Active Fluid-Bed (CAFB) process. The process was originally conceived at the Esso Petroleum Company, Ltd., Abingdon, UK (ERCA), as a fluidized-bed gasification process to convert heavy fuel oils to a clean, medium heating-value fuel gas for firing in a conventional boiler. Westinghouse, under contract to EPA, completed an initial evaluation of the process in 1971.[1] Conceptual designs and cost estimates were prepared for new and retrofit utility boiler applications using heavy fuel oil. Westinghouse continued the process evaluation from 1971 to 1973 and formulated an atmospheric pollution control demonstration plant program for retrofit of a utility boiler utilizing a high-sulfur, high-metals content fuel oil (for example, vacuum bottoms).[2] The CAFB process represented an attractive option for use of these low-grade fuels, for which pollution control using hydrodesulfurization or stack-gas cleaning was not economical. Application of a pressurized CAFB concept with combined-cycle power plants was also assessed.[2] Experimental support work was initiated between 1971 and 1973 to investigate two areas of concern - sorbent selection and spent sorbent processing - to achieve an acceptable material for disposal or utilization. The preliminary design and cost estimate for a 50 MWe demonstration plant at the New England Electric System (NEES) Manchester Street Station in Providence, RI were completed in 1975.[3] Commercial plant costs were projected and development requirements identified. Experimental support of the sulfur removal system continued in order to provide a basis for

the detailed plant design. A number of design and operating parameters from the preliminary design study that required further development were identified. The environmental impact of the disposal of unprocessed and processed spent sulfur sorbent has continued to be an area requiring further study. This report presents the results of a test program carried out from 1976 to 1979 to obtain data for assessing the potential environmental impact of disposal.

Additional support work carried out under the present contract (68-02-2142) includes:

- Sorbent selection[4,5]
- Processing spent sorbent to minimize environmental impact[4]
- Solids transport between adjacent CAFB fluidized beds[6]
- Engineering evaluation of the CAFB process[7]

ABSTRACT

The chemically active fluidized-bed (CAFB) process is being developed to convert high-sulfur heavy oils and low-grade coal to clean, medium heating-value fuel gas in conventional boilers. The disposal of the spent sorbent, which consists of varying amounts of CaO, CaS, and $CaSO_4$, may cause environmental concerns associated with potential air, water, odor, and heat pollution. The spent sorbent can be further processed to reduce its environmental impact by methods including dry sulfation, dead-burning, room-temperature fly ash blending, high-temperature processing, and slurry carbonation. A laboratory experimental program has been carried out to investigate three major areas: residue characterization, leaching property, and thermal activity. The results from tests on solid residues from the Esso Research Centre, Abingdon, UK (ERCA) pilot plant indicate that the CAFB spent sorbent residue may be hazardous because of its sulfide content. Test results indicate that nonhazardous disposal of the residue can be achieved by processing the spent sorbent. The environmental impact of CAFB residue disposal is also compared with results of conventional power plant residues: flue gas desulfurization residues (FGD) and lignite ash. Federal regulations and guidelines on solid waste disposal, including the recently enacted Resource Conservation and Recovery Act, have been reviewed to assess their impact on CAFB solid residue disposal.

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NOMENCLATURE

ΔT_5 = reactivity coefficient

BOD = biochemical oxygen demand

CAFB = chemically active fluidized bed

COD = chemical oxygen demand

CSO = Columbus Southern Ohio Company

DLC = Duquesne Light Company

DWS = drinking water standards

EDAX = energy dispersive analysis by X-ray

EMA = electron microprobe analysis

ERCA = Esso Research Centre, Abingdon, UK

FBC = fluidized-bed combustion

FGD = flue gas desulfurization

LGE = Louisville Gas and Electric Company

MATE = Minimum Acute Toxicity Effluent

MEG = Multimedia Environmental Goals

NIPDWR = National Interim Primary Drinking Water Regulations

RCRA = Resource Conservation and Recovery Act

SAM = Source Analysis Model

SEM = scanning electron microscopy

TDS = total dissolved solids

TEP = toxicant extraction procedure

NOMENCLATURE (Cont)

TGA = thermogravimetric analysis

TOC = total organic carbon

TUGCO = Texas Utility Generating Corporation

USPHS = United States Public Health Service

WHO = World Health Organization

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SUMMARY

Westinghouse has developed an experimental testing program to determine the environmental impact of the disposal of CAFB residue, concentrating its efforts on three major areas -- residue characterization, leaching property investigation, and potential thermal pollution.

We have reviewed the environmental laws, including up-to-date development of the regulations and guidelines under the authority of the Resource Conservation and Recovery Act.[8]

Actual CAFB residues from ERCA's gasifier, regenerator, cyclone, and stack were used in this study. Materials processed by dry sulfation, dead-burning, room-temperature ash blending, high-temperature compacting, and slurry carbonation were also tested to evaluate the effect of further processing.

On the basis of laboratory testing results, we judged that unprocessed CAFB spent sorbent would be environmentally unacceptable for direct land disposal. Environmental acceptability, however, can be achieved by further processing based on the available test data. Table 1 summarizes the degree to which negative environmental impact can be reduced by use of four of the processing alternatives for spent sorbent from the CAFB gasification process. We believe the leaching tests performed result in severer projections of environmental impact than will be encountered in practice. Since there are no guidelines for leachate qualities at the present time, we have compared results with drinking water standards and the leachate characteristics of natural gypsum.

The drinking water standards in this investigation, however, are used only in an effort to put data into perspective until EPA guidelines are established and should not be construed as suggesting that the leachate must necessarily meet drinking water standards. These standards

of course, are extremely conservative; a leachate dilution/attenuation factor of 10 is currently being considered in the proposed regulations under Section 3001 of the Resource Conservation and Recovery Act of 1976[8] (RCRA) by the Hazardous Waste Management Division of the Office of Solid Waste, EPA.

The major environmental concerns with direct disposal are heat release, sulfide, pH, calcium, SO_4, and TDS. The major environmental concerns with disposal after processing are pH, calcium, SO_4, and TDS. On the basis of these results, spent sorbent processing will be required for nonhazardous disposal. Four processing options were investigated. A comparison of the environmental impact is summarized in Table 1. On the basis of environmental impact, the high-temperature processing or dry sulfation options are the recommended processes, followed by dead-burning and low-temperature fly ash blending. There are advantages and disadvantages to each method of processing, and the decision for each application will be based on the balance of technical, environmental, and economic factors. For example, the high-temperature processing option requires a high energy consumption and may only be selected if it can result in utilization of the product material. Of course, site selection, design and management of the disposal task based on the site-specific hydrology, geology, climate, and soil composition are critically important to the success of solid waste disposal practice. Selection of the proper processing method to reduce surface area and permeability and to improve the heat-release and leaching properties can greatly simplify the disposal management task.

Pending implementation of EPA criteria with which to assess the environmental acceptability of the disposal of CAFB residues, the chemical, physical, and leaching properties of the spent CAFB material are compared with the residues from conventional coal-burning power plants with flue gas desulfurization processes (FGD).

Table 1

COMPARISON OF ENVIRONMENTAL IMPACT OF PROCESSED AND UNPROCESSED CAFB SPENT SORBENTS

Environmental Parameters / Processing	pH	Total Dissolved Solids	Sulfide [a]	Sulfate	Calcium	Trace Metal	Heat Release [a] (3gm/20 ml)	Total Organic Carbon [a]
Unprocessed CAFB	u	u	u	u	u	u	ΔT = 18°C	u
Dry-Sulfation	+	+	+	0	+	0	ΔT = ND < 0.2°C	0
Dead-Burning	0	0	+	+	+	0	ΔT = ND < 0.2°C	0
Rm-temp. Processing	0	0	+	0	+	0	ΔT = ND < 0.2°C	0
Hi-temp. Processing	+	+	+	+	+	0	ΔT = ND < 0.2°C	0

Note: u Unprocessed CAFB Leachate Characteristics
+ Improved From u Value
0 No Significant Change From u Value

Do Not Meet Either The Drinking Water or Gypsum Leachate Criteria

Pass Gypsum Leachate Criteria But Not Drinking Water Standards

Pass Both Drinking Water and Gypsum Leachate Criteria

(a) No Drinking Water Standards Exist

A preliminary comparison of the environmental impact of the disposal of unprocessed CAFB solid wastes and FGD sludge residues from varying processing systems suggests that the disposal of the CAFB solid waste may cause comparable (due to chemical properties), perhaps less negative (due to physical properties), environmental effects than the disposal of the residue from currently commercialized FGD processes.

This assessment is based on results from a continuing program that is, however, limited by the investigation of spent CAFB materials from a pilot-scale operation. These conclusions are considered preliminary and should be reassessed as more representative samples become available from a larger scale plant.

1. INTRODUCTION

The CAFB (Chemically Active Fluidized Bed) gasification process, in which limestone or dolomite removes the sulfur from fuel gas during the gasification process, wa developed to permit the utilization of high-sulfur residual fuel oil or refinery bottoms in conventional boilers by producing a low-sulfur fuel gas. Coal is also being investigated as a fuel. The process can be operated as a once-through limestone sorbent system, a sorbent regeneration/sulfur recovery system, or a sorbent regeneration system without sulfur recovery by capturing the sulfur-rich gas from the regenerator with the spent stone. The spent stone from each system alternative can be processed to minimize the environmental impact of the waste stone for disposal or to provide material for potential market utilization.[3,9]

Under contract to the U. S. Environmental Protection Agency (EPA), Westinghouse has carried out laboratory support work on sulfur removal, solid transport, and the environmental impact of residue disposal.[3,9] Esso Research Centre, Abingdon, England (ERCA) is carrying out pilot-scale tests to investigate sulfur removal.[10] At San Benito, Texas, a 10 MW demonstration plant has been retrofitted by Foster Wheeler Energy Corporation and Central Power and Light Co., and larger-scale testing has begun.[11]

The CAFB gasification/desulfurization process produces a dry, partially utilized limestone (or dolomite) with particles up to 6000 μm in size. The composition of the sorbent for disposition will depend on the characteristics of the original stone, the fuel feed, the selection

of the sorbent processing system, and the process operating conditions. Spent sorbent compositions for the once-through and regenerative operating modes are:

	Solids Composition, wt % Regenerative (regenerator solids)	 Once-through (gasifier solids)
CaO	85-95	50-75
CaS	2-5	25-50
$CaSO_4$	2-4	∿1
Inerts	1-10	1-10

The disposal of this solid may be accomplished by a variety of methods. Several processing alternatives have been developed to convert calcium oxide (CaO) and calcium sulfide (CaS) to an environmentally acceptable form for disposal or further utilization. Dry sulfation and dead-burning are examples of dry processing systems; slurry carbonation is an example of the wet methods investigated.[3,9]

Among the factors that will affect the disposition of the spent sorbent are the quantity of spent sorbent, its chemical characteristics, regulations, geographical location, and the size of the market for the respective applications. The environmental impact of any disposed material is a function of its physical and chemical properties and the quantity involved. Potential water pollution problems in many cases can be predicted by chemical properties such as solubility, the presence of toxic metals, and the pH of leachates. The disposal of spent stone from the CAFB gasification process may create air pollution or odor nuisance (e.g., hydrogen sulfide [H_2S], depending on the amount of CaS present. Heat may be released on hydration of CaO. Potential water pollution may be introduced from the runoff leachates caused by the rainfall and naturally occurring subsurface flow through the landfill site. An experimental testing program on stone analysis, leaching properties, heat release properties, landfill properties, and air emission has been carried out to obtain this information. The assessment reported here is limited to the environmental impact from land disposal of unprocessed and processed spent sorbent. The processing work is discussed elsewhere.[12]

2. REGULATIONS/CRITERIA

Under the authority of the Clean Air Act of 1970, the EPA promulgated regulations on standards of performance for new stationary sources of air pollution.[13] Specifically, subpart B established standards of performance for fossil-fuel-fired steam generators of more than 263.75 GJ/hr (250 million Btu/hr) and established the standards for sulfur dioxide (SO_2) emission. The alternatives available for compliance with SO_2 standards are:

1. To burn low-sulfur fuels
2. To remove the SO_2 from the exhaust gas with FGD systems
3. To use alternative technologies.

As an example of the third alternative, the chemically active fluidized-bed gasification process employs calcium-based sorbent for sulfur removal that results in the production of dry, partially utilized sorbent and ash as solid residue for disposal. The environmental standards for solid residue disposal from CAFB systems have not been established. Two environmental laws that affect solid waste disposal are the Resource Conservation and Recovery Act (RCRA) of 1976 (the Solid Waste Disposal Act of 1965, as amended by P.L. 94-580, 1976),[8] and the Federal Water Pollution Control Act of 1972 (Public Law 92-500, 1972, as amended by Clean Water Act, P.L. 95-217, 1977).[14,15] Eventually, disposal guidelines are to be promulgated by EPA under the authority of the former.

As a result of the Clean Air Act, the Water Pollution Control Act, and other federal and state laws respecting public health and the environment, greater amounts of solid waste have been created. Similarly,

inadequate and environmentally unsound practices for the disposal or use of solid waste may create greater amounts of air and water pollution and other problems for the environment and for health. Among the objectives of RCRA are the protection of health and the environment and the conservation of valuable material and energy resources by:

- Providing technical and financial assistance to state and local governments and interstate agencies for the development of solid waste management plans
- Providing training grants in occupations involving the design, operation, and maintenance of solid waste disposal systems
- Prohibiting future open dumping on the land and requiring the conversion of existing open dumps to facilities that do not pose a danger to the environment or to health
- Regulating the treatment, storage, transportation, and disposal of hazardous wastes that have adverse effects on health and on the environment
- Providing for the promulgation of guidelines for solid waste collection, transport, separation, recovery, and disposal practices and systems
- Promoting a national research and development program for improved solid waste management and resource conservation techniques.

The passage of RCRA closed the legislative loop of environmental laws (air/water/solid) and created a new level of control over solid waste disposal. Of special concern are the regulations to be promulgated under Subtitle C - Hazardous Waste Management.[16-18] Table 2 summarizes the currently proposed criteria for hazardous waste identification and those that are being considered for future ruling. Of the characteristics currently proposed for hazardous waste (ignitability, corrosivity, reactivity and toxicity), toxicity and reactivity cause the most concern.

Table 2

HAZARDOUS WASTE CRITERIA (RCRA SECTION 3001)

Characteristics	Status	Comment
1. Ignitability	Proposed Dec. 18, 1978 in Fed. Reg.; scheduled to be promulgated Dec. 31, 1979. Not intended to be static; to be reviewed periodically.	Current proposed regulations apply only to liquid waste pH $\geq$12 or $\leq$3, but proposed regulations may change.
2. Corrosivity		
3. Reactivity		"Sulfide bearing waste which can generate toxic gases"...or, "reacts violently with water"... . Some uncertainty may arise from the interpretation of this qualitative statement, especially with regard to regenerative, PFBC residue.
4. Toxicity		A waste is hazardous if its "EP" leachate exceeds 10X primary DWS.
5. Radioactivity	Advanced Notice for Proposed Rulemaking, Dec. 18, 1978. Comments/information invited.	
6. Generic Activity		
7. Bioaccumulation	To be proposed in Fed. Reg. no sooner than 1 yr. from the Advance Notice date, i.e., Dec. 18, 1979.	
8. Additional Aspects of Toxicity		

A waste is considered toxic and, therefore, hazardous if its eluent from the "extraction procedure" (EP, proposed in Federal Register, Dec. 18, 1978) contains trace elements exceeding ten times the primary drinking water standards. Because of the low levels of trace elements

exhibited by the CAFB leachates, we expect that the CAFB solids would not be toxic. The unprocessed CAFB residue, however, may be considered "reactive" because of its sulfide content. This is by no means conclusive. Should the CAFB solids be determined to be hazardous waste under RCRA 3001, we would expect them to be classified under the "special waste" category under the regulations of RCRA Sec. 3004 for "utility waste." On the other hand, they could be processed (and we have shown that this can be done) to render them nonhazardous and, therefore, subject to the regulations and criteria under RCRA Sec. 4004 for nonhazardous waste disposal[19] and proposed guidelines under RCRA Sec. 1008 for location, design, construction, operation, and maintenance of solid waste land disposal facilities.[20]

The primary environmental concern with solid waste disposal is the potential ground and surface water contamination caused by leachate run-off or seepage. The federal regulation that most nearly relates to a limit on seepage water quality is the EPA's "Alternative Waste Management Techniques for Best Practical Waste Treatment"[21] under the authority of the Federal Water Pollution Control Act of 1972 amended by the Clean Water Act of 1977. These criteria, which apply to publicly owned treatment and land application of waste water, state that the groundwater, resulting from land applications of waste water, shall be limited to the maximum contaminant levels contained in the National Interim Primary Drinking Water Regulations (NIPDWR)[22] or to the existing concentration if the latter is greater. If the groundwater is to be used for other than a drinking water supply, "the ground water (sic) criteria should be established by the Regional Administrator." In contrast to the United States Public Health Service (USPHS) Drinking Water Standards (DWS), 1962,[21] which limit sulfate and chloride to 250 mg/ℓ each (and many others, e.g., copper, iron, manganese, nickel, tin, and zinc), no limits are given in the NIPDWR for these substances. These and other substances, however, may be included in secondary standards, when issued.

In anticipation of such forthcoming criteria, the chemical characteristics of leachates from leaching experiments are compared with the drinking water standards set by NIPDWR,[22] USPHS Drinking Water Standards,[23] and the World Health Organization (WHO) Potable Water Standards.[24] Of course, these standards are extremely conservative; a leachate dilution/attenuation factor of 10 is currently being considered in the regulation draft under Section 3001 of RCRA by the Hazardous Waste Management Division of the Office of Solid Waste, EPA.[17] Note that the drinking water standards are used in this investigation only in an effort to put data into perspective in the absence of EPA guidelines and should not be construed as suggesting that the leachate must necessarily meet drinking water standards. Although the guidelines for the power plant effluents[25] are not applicable to the disposal of dry spent sorbent from the CAFB process, they are used as additional references in this investigation. Table 3 lists the selected water quality criteria for leachate comparison.

Currently, EPA-IERL-RTP is developing Multimedia Environmental Goals (MEG)[26] and Minimum Acute Toxicity Effluent (MATE)[27] for use in the environmental assessment of rapid effluent screening. MATE values are being developed on the basis of health and ecology for land, water, and air. EPA-IERL-RTP/EACD (Energy Assessment Control Division) is also developing Source Analysis Models (SAM) based on comparison with MEG and MATE values. SAM/IA ranks effluent by "degree of hazard" and "toxic unit discharge rate,"[28] and provides a standardized methodology for environmental assessment.

Existing air pollution control regulations limit the SO_2 emission level discharged by fossil fuel power plants. One commercialized process for SO_2 removal is flue gas desulfurization (FGD), which generates large quantities of sludge and has received considerable attention environmentally. A recently published EPA report by SCS Engineers entitled "Data Base for Standards and Regulations Development for Land Disposal of Flue Gas Cleaning Sludges[29] concluded that the characteristics of FGD sludge set the need for regulation and recommended that

Table 3

SELECTED WATER QUALITY CRITERIA

Substance	Drinking Water Standards, mg/ℓ				Effluent Guidelines and Standards for Steam Electric Power Generation,[25] mg/ℓ
			WHO[24]		
	NIPDWR[22]	USPHS[23]	Highest Desirable Level	Maximum Permissible Level	
Ag	0.05	0.05			
As	0.o5	0.05	0.05	0.05	
Ba	1.0	1.0			
Ca			75	200	
Cd	0.01	0.01	0.01	0.01	
Cr	0.05	0.05 (Cr^{+6})			0.2
Cu		1.0	0.05	1.5	1.0
Fe		0.3	0.1	1.0	1.0
Hg	0.002		0.001	0.001	
Mg			30	150	
Mn		0.05	0.05	0.5	
Ni		2.0			
Pb	0.05	0.05	0.1	0.1	
Se	0.01	0.01	0.01	0.01	
Sn		1.0			
Zn		5.0	5.0	15	1.0
SO_4		250	200	400	
Cl		250	200	600	
NO_3	10 (as N)	45	45	45	
F	1.4 to 2.4	1.7	1.7	1.7	
pH (pH unit)			7.0 - 8.5	6.5 - 9.2	6.0 - 9.0
TDS		500	500	1500	

regulations allow for site-specific factors as well as sludge characteristics. Important disposal site characteristics to be considered for regulatory action are present and projected land use, topology, hydrology, and meteorology.

Because of the wide variation in the characteristics of solid wastes in general, weather, soils, topography, groundwater from site to site, and nearby stream guality and flow characteristics, permits are currently being awarded on a site-specific basis. Eventually, state regulations will apply as a result of the RCRA,[8] but these regulations will not be enacted until federal standards are promulgated. Depending on the actual site selected for disposal, the leachates would have to meet the water quality criteria for the specific water use.[30] Furthermore, the success of a land disposal application depends, above all, on the design, construction, and operation of a specific disposal site based on the geology, hydrology, and meteorology of that particular site.

3. EXPERIMENTAL TESTING PROGRAM

SAMPLES

Samples investigated to leach the environmental impact of land disposal fall into three categories.

Unprocessed CAFB Residue[10]

Residues from the CAFB pilot plant at ERCA were used. These included spent gasifier, regenerator, cyclone, and stack fines. Table 4 summarizes the unporcessed ERCA residues tested and the fuel and sorbent used for each run.

Processed CAFB Residue[3,9,12]

Various techniques for further processing were used on the spent sorbent. Samples tested for their environmental impact included those processed by the most promising methods: dry sulfation, dead-burning, room-temperature fly ash blending, and high-temperature compacting. They are listed below:

- DS-mix - CAFB-7 spent sorbent processed by dry sulfation in a 2.5-cm bench-scale fixed-bed reactor
- CAFB-903 - CAFB-9 spent sorbent processed by dry sulfation in a 10-cm fluidized-bed unit
- CAFB-904 - CAFB-9 spent sorbent processed by dry sulfation in a 10-cm fluidized-bed unit, then separated by particle size to two fractions which achieved different degrees of sulfation
- DB163 to 171 - nine CAFB-9 spent sorbents processed by dead-burning at three different temperatures for three different durations

Table 4

CAFB SPENT SORBENTS TESTED

CAFB-Run	Fuel	Sorbent
CAFB-7	High-S residual oil	Denbighshire limestone + BCR 1359 limestone
CAFB-8	High-S residual oil	BCR 1359 limestone
CAFB-9	High-S residual oil	BCR 1359 limestone + Aragonite
CAFB-10	High-S residual oil + bitumen	BCR 1359 limestone
CAFB-10A	High-S residual oil + coal and lignite	BCR 1359 limestone
CAFB-11	Lignite	BCR 1359 limestone

- DB44 μm - six CAFB-9 spent sorbents of -44 μm size processed by dead-burning at two different temperatures for three different durations
- DB-66+88 μm - six CAFB-9 spent sorbents of -66+88 μm size processed by dead-burning at two different temperatures for three different durations
- Room temperature 4A, 4B, and 4C air cured for 7, 14, and 28 days - nine solid compacts prepared from three mixtures of CAFB-9 spent sorbent and fly ash, and air cured in water for three lengths of time
- Hi-temperature 75-CF-22, 75-CF-26, 65-CF-30 - three solid compacts prepared by hot pressing mixtures of CaS, CAFB-9 spent sorbent, and $CaSO_4$ with fly ash at 1050°C and 33,000 MPa (4800 psi).

Reference Material

The following reference materials were tested:

- FGD residue. Unprocessed and processed SO_2 scrubber sludges from conventional power plants with FGD systems provide a comparison of power plant residue with a currently commercialized process.
- Lignite Ash.[31] Lignite ash from (TUGCO) serves as a reference for lignite ash for residues from CAFB gasification of lignite.
- Valley Builder Supply Block.[31] Representative blocks and aggregates manufactured by Valley Builder Supply, a potential contractor to utilize the CAFB spent sorbent from the CAFB demonstration plant at San Benito, Texas, were tested to provide reference for processed CAFB spent sorbent.
- Gypsum. Iowa ground gypsum No. 114 was used to provide a reference for $CaSO_4$ leachability because of the large amount of $CaSO_4$ present in the spent CAFB sorbents.

EXPERIMENTAL PROGRAM AND TEST METHODS

The environmental impact of any disposed material is a function of its physical and chemical properties as well as of the quantity involved. Potential water pollution problems can be predicted from the chemical characteristics of leachates, such as pH, specific ion concentrations, trace element dissolution, and total dissolved solids (TDS). Disposal of the CAFB solid wastes may also create air pollution, odor nuisance, and heat-release problems. To assess the environmental impact of CAFB solid waste disposal and the suitability of waste material as landfill, physical and chemical characteristics of the residue, leaching, and heat-release properties were investigated.

Characterization

Chemical, physical, and morphological characterization of the spent bed and carry-over material was carried out by optical microscopy, scanning electron microscopy (SEM), energy dispersive analyses by X-ray (EDAX), electron microprobe analysis (EMA), X-ray diffraction, thermogravimetric analysis (TGA), emission and atomic absorption spectroscopy, and wet chemical methods.

Leaching Tests

At this time, there is no standard EPA leaching test with which the potential environmental contamination from a solid waste can be assessed. A standard test has been proposed by EPA in the Federal Register "Hazardous Waste Guidelines and Regulations"[18] under the authority of RCRA Sec. 3001 to identify hazardous waste. We expect this test, entitled "extraction procedure"(EP), to be promulgated in December 1979.

Parallel to the EPA effort, ASTM committee 19.12 (subcommittee 19.1203) is also developing a standard leaching test[32] for solid waste materials. A 48-hour shake method using either type IV reagent water (ASTM D-1193 or pH = 4.5 sodium acetate-acetic acid buffer is proposed. A shake test is proposed by both organizations.

In this study leachates were induced by the shake test that Westinghouse developed prior to the EPA and ASTM efforts,[9,33,34] unless otherwise specified. Samples of waste stones were mixed with deionized water in Erlenmeyer flasks at room temperature. An automatic shaker capable of 70 excursions per minute was used to agitate the mixtures. Among the parameters investigated were sorbent/water loading, sample mixing time, and pH of the leading medium. The supernatants resulting from this operation were filtered, and the filtrate was determined for pH, specific conductance, TDS, calcium, magnesium, sulfide, sulfate, trace metal ion and anion concentrations, and total organic carbon (TOC) content. The solid samples before and after the leaching operation were also analyzed for their chemical and physical characteristics. Since $CaSO_4$ is a major constituent of the waste stone, and leachates contained high calcium and sulfate concentrations, a naturally occurring gypsum was tested under similar leaching conditions for comparison.

Two shake procedures have been employed. These are described below.

- Continuous shake test. It establishes equilibrium conditions between the solid and its aqueous surrounding and provides the worst possible case with respect to contamination release. This method has been used by Westinghouse since 1975 as one of the screening tests for determining leaching properties of CAFB spent solids. Typically, a 1:10 solid-to-water ratio is used.

- Intermittent shake test. A series of ten to fifteen cycles of a 72-hour shake test was adopted as part of the leachability study to provide leaching rate, aging effect, and long-term leachability of the worst case and to make possible the calculation of "total fraction leached" for any specific ion or for TDS as a function of total leach time or total leachate passing the sample. Leachates were analyzed at the end of each interval, and a fresh charge of ionized water was added for each 72-hour leach cycle. Typically, a 1:3 solid-to-water ratio was used.

Both shake tests are more severe than conditions anticipated under actual land disposal; results from the shake tests are expected to project the worst.

Activity Tests

No standard EPA activity test exists. Under Sec. 3001 of RCRA, EPA's Hazardous Waste Management Office is currently developing test methods for reactivity criteria as an effort to define hazardous waste.[17] Their tests concentrate on hazardous properties such as explosiveness and chemical and mechanical instability but do not apply to residual lime.[35]

The activity of residual lime in spent CAFB materials can be determined by its heat release property on contact with water, as the hydration reaction of CaO is extremely exothermic.[36] Literature on lime reactivity and slaking rate has been reviewed, including the ASTM C110[37] for the slaking rate of quicklime (CaO), Murray's study of lime reactivity as a function of porosity and shrinkage characteristics during calcination,[38] and American Water Works' standard on lime for water treatment.

The heat release activity of CAFB residue in this study was measured calorimetrically. The temperature rise of a solid/water system containing free CaO is a function of the solid/water ratio. In our experimental effort to establish a screening test for the residual activity in spent CAFB solids produced under varying processing conditions, a solid/water proportion of 3 g to 20 ml (which is in the bulk range specified by the ASTM-C110 test and by Murray's work) was found empirically to provide much better repeatability than that from a higher solid/water ratio that would give greater temperature rise but would lack reproducibility, probably due to local heating. Higher solid/water ratios were also used, nowever, because they provide higher sensitivity and simulate rainfall onto the disposed solid.

Chromel-alumel thermocouples were used to monitor the temperature rise in the stone/water system with an Omega cold junction compensator and a millivolt recorder. The heat release tests were conducted on the actual spent sorbent and on carry-over fines from the CAFB pilot unit at ERCA. Calcined and uncalcined limestone and dolomite samples were also tested for comparison.

RESULTS

Unprocessed Residue[10]

The actual CAFB residues from ERCA pilot-scale runs were tested in this work. These can be further grouped as shown below. Table 5 summarizes the typical compounds present as identified by X-ray diffraction.

CAFB-7, 8, 9 Regenerator Material

Three batches of actual regenerator spent sorbents using residual oil as the fuel were tested. Table 6 summarizes the chemical analyses. Leaching tests were carried out under both aerobic and anaerobic conditions - in other words, under air and nitrogen atmospheres, respectively. The oxidation and leachability of sulfide ions

Table 5

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SPENT SORBENT CHARACTERIZATION BY X-RAY DIFFRACTION

Sample	Fuel	Physical Separation	Chemical Composition						Others
			CaO	$Ca(OH)_2$	CaS	$CaSO_4$	$CaCO_3$	SiO_2	
CAFB-8 Gasifier Bed	Resid. oil	White particles	--	Major	Minor	--	--	--	
CAFB-8 Gasifier Bed	Resid. oil	Black particles	Minor	Trace	Major	--	--	--	
CAFB-8 Regular Bed	Resid. oil	White	Major	Major	--	Major	--	--	
CAFB-8 Regular Bed	Resid. oil	Black	--	Major	Major	--	Trace	--	
CAFB-8 Stack Fines	Resid. oil	No separation	Major	Major	--	Minor	Trace	Minor	
CAFB-10A Gasifier Bed	Resid. oil + coal + lignite	No separation	Major	Trace	--	Minor	--	--	
CAFB-11 Regular Bed	Lignite		Major	Minor	Trace	Trace	--	Minor	Trace Foresterite Spinel
CAFB-11 Cyclone	Lignite		Major	Major	--	--	--	Major	Fe_3O_4 Spinel
CAFB-11 Stack Fines	Lignite		--	--	Trace	Trace	Trace	Major	Trace α-Fe_2O_3 Al_2O_3 and Fe_3O_4 Spinel

Table 6

CHEMICAL ANALYSIS OF CAFB SPENT SORBENTS FROM THE REGENERATOR

	CAFB-7, %	CAFB-8, %	CAFB-9, %
Ca	66.5	60.5	64.3
$S^{=}$	1.25	3.89	2.24
$SO_4^{=}$	2.98	2.31	3.07

were affected by the oxygen partial pressure in the system. Table 7 summarizes the chemical characteristics of the leachates. Table 8 summarizes the trace metal contents in the spent regenerator sorbents and their leachates. Results showed that:

- The leachability of trace metal ions is not expected to cause water pollution.
- The leachates are alkaline with pH = 12.8.
- Concentrations of calcium, sulfate, sulfide, and TDS as well as pH are major concerns.
- Total dissolved ions are higher for the anaerobic leaching, as indicated by the specific conductance of the leachates.
- Sulfide is higher in the anaerobic leachates and sulfate is higher in the aerobic case when all other conditions are identical. This is reasonable because part of the dissolved sulfides may be oxidized to sulfate under aerobic mixing conditions.
- Gaseous H_2S evolution from leachates over 240 hours constitutes less than 1 percent of the total sulfide in the stone. Note, however, that these tests were conducted in deionized water at room temperature. In the case of acid rainfall onto the disposed sulfide-containing stone, the H_2S evolution would probably be higher.
- Further processing of the spent stone is deemed necessary in order to render it environmentally suitable for disposal.

Table 7

LEACHING RESULTS OF SPENT CAFB REGENERATOR SORBENTS

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Regenerator Spent Sorbents	Experiment	Conditions	Chemical Characteristics of Leachates					Gaseous S, % of S in Solid
			pH	Specific Conductance, $\mu mhos\text{-}cm^{-1}$	Ca, mg/ℓ	$S^{=}$, mg/ℓ	$SO_4^{=}$ mg/ℓ	
CAFB-9	Stone loading	4 g/200 ml/24 hr, aerobic	12.6	6,300	824	106	346	
		20 g/200 ml/24 hr, "	12.7	7,390	1,368	435	1,037	
		40 g/200 ml/24 hr, "	12.6	8,900	1,824	576	1,325	
		80 g/200 ml/24 hr, "	12.5	1,340	3,496	2,560	1,536	
		4 g/200 ml/24 hr, anaerobic	12.64	6,900	928	166	307	
		20 g/200 ml/24 hr, "	12.64	8,380	1,512	659	614	
		40 g/200 ml/24 hr, "	12.5	9,580	1,952	928	1,075	0.054%
		80 g/200 ml/24 hr, "	12.5	14,200	3,784	5,000	2,016	0.054%
	Mixing time	20 g/200 ml/6 hr, aerobic	12.5	6,790	936	230	422	
		20 g/200 ml/24 hr, "	12.7	7,890	1,368	435	1,037	
		20 g/200 ml/96 hr, "	12.6	8,920	1,860	627	1,555	
		20 g/200 ml/150 hr, "	12.8	9,180	1,936	1,062	1,843	
		20 g/200 ml/214 hr, "	12.9	9,330	2,064	883	2,016	
		20 g/200 ml/6 hr, anaerobic	12.6	7,060	984	214	461	
		20 g/200 ml/24 hr, "	12.7	8,380	1,512	659	614	
		20 g/200 ml/96 hr, "	12.6	9,840	2,096	1,338	1,286	
		20 g/200 ml/150 hr, "	12.8	10,490	2,344	1,734	1,277	< 0.3%
		20 g/200 ml/214 hr, "	12.6	10,710	2,440	1,888	1,210	< 1%
CAFB-7	Stone loading	1 g/250 ml/24 hr, aerobic	12.8	6,040	668	6.4	77	
		25 g/250 ml/24 hr, "	12.8	6,600	760	22.4	153	
		10 g/250 ml/24 hr, "	12.8	7,630	1,005	73.5	556	
		25 g/250 ml/24 hr, "	12.8	8,380	1,280	185	1,035	
		50 g/250 ml/24 hr, "	12.8	7,170	1,576	485	1,990	
	Mixing time	25 g/250 ml/ 1 hr, "	12.7	7,750	920	12.8	220	
		25 g/250 ml/ 3 hr, "	12.7	7,610	938	32.0	345	
		25 g/250 ml/ 6 hr, "	12.8	7,810	1,000	54.3	480	
		25 g/250 ml/17 hr, "	12.8	8,140	1,175	191.5	844	
		25 g/250 ml/24 hr, "	12.8	8,380	1,280	185	1,035	
		25 g/250 ml/48 hr, "	12.8	8,735	1,453	329	1,380	
CAFB-8	Mixing time	10 g/100 ml/48 hr, aerobic	12.3	9,150	1,624	–	931	
		10 g/100 ml/100 hr, "	12.1	9,700	1,724	432	1,548	
		10 g/100 ml/240 hr, "	12.1	10,360	2,096	264	1,622	
		10 g/100 ml/432 hr, "	12.4	10,130	2,176	744	1,297	
		10 g/100 ml/48 hr, anaerobic	12.3	8,580	1,352	784	1,225	
		10 g/100 ml/100 hr, "	12.1	9,930	1,752	936	1,000	<0.01%
		10 g/100 ml/240 hr, "	12.1	11,000	2,064	1072	1,211	<0.01%
		10 g/100 ml/432 hr, "	11.7	10,690	2,232	1376	1,410	<0.01%

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Table 8

TRACE METAL ELEMENTS IN THE UNPROCESSED CAFB REGENERATOR SPENT SORBENTS AND THEIR LEACHATES

Samples / Elements	Spent Sorbent, wt%		Leachates, mg/ℓ		DWS *
	CAFB-9	CAFB-8	CAFB-9	CAFB-8	
Ag	< 0.0002	< 0.01	ND < 0.02	< 0.03	0.05
Al	0.3	0.07	< 0.1	< 1	
As	< 0.02		ND < 0.1	< 0.05	0.05
B	< 0.002	ND < 0.01	0.3	0.03	
Ba			0.1		1.0
Be	< 0.0001		ND < 0.01	<< 0.1	1.0
Bi	< 0.0007	ND < 0.01	ND < 0.04	< 0.03	
Ca	> 10	> 10	> 1000	> 1000	
Cd	< 0.007	ND < 0.03	ND < 0.3	< 0.03	0.01
Co	< 0.002	ND < 0.01	ND < 0.1	< 0.1	
Cr	0.002	ND < 0.03	ND < 0.05	< 0.03	0.05
Cu	< 0.002	< 0.01	ND < 0.1	0.08	1.0
Fe	0.2	0.1	0.1	0.03	0.3
Hg				< 0.001	0.002
Li		< 0.03	< 0.1		
Mg	0.8	0.33	0.4	< 1	
Mn	0.02	0.05	ND < 0.02	< 0.03	0.05
Mo	0.007	ND < 0.01	0.4	0.08	
Na		< 0.1	1		
Ni	0.1	0.03	ND < 0.02	< 0.1	2.0
Pb	< 0.007	ND < 0.01	ND < 0.05	< 0.1	0.05
Se			ND << 1	< 0.01	0.01
Si	1	0.3	0.4	0.2	
Sn	< 0.002	ND < 0.03	ND < 0.2	< 0.1	1.0
Sr			> 10		
Ti	0.01	0.02	ND < 0.2	< 0.03	
V	1	0.3	ND < 0.05	< 0.03	
Zn	< 0.007	ND < 0.03	ND < 0.5	< 1	5.0
Zr	< 0.001	ND < 0.03	ND < 0.2	< 1	
Sb		ND < 0.03		< 0.1	

ND – Not Detectable

* DWS – U.S. Public Health Service Drinking Water Standards (USPHS 1972)

National Interim Primary Drinking Water Regulations (NIPDWR, 1976)

World Health Organization Drinking Water Standards (WHO, 1971)

Leaching tests using the intermittent shake method and activity tests are discussed in later sections.

CAFB-8 Gasifier Material

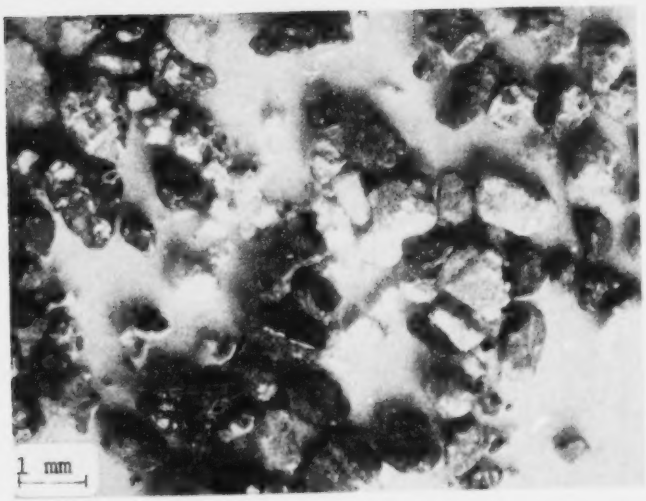
Both the gasifier and the regenerator spent sorbents are granular, with varying color shades, as shown in Figure 1. They gradually disintegrate into grayish powder on contact with moisture in the air. The spent sorbent after leaching becomes a white-to-gray powder consisting primarily of calcium carbonate ($CaCO_3$) and slaked lime ($Ca(OH)_2$). Although the spent sorbent from the gasifier is not expected to be disposed of directly, it is also tested for its leaching behavior. Table 9 summarizes the results. As expected, results indicated less desirable characteristics than those from the leachate of the regenerator stone, which is also judged unsuitable for direct disposal.

CAFB-8 Stack Fines

Effort was directed toward characterizing the stack fines since the particulate emission from the CAFB process is a potential concern.

Scanning electron microscopy (SEM) and energy dispersion analysis by X-ray (EDAX) were used for chemical and physical characterization. Figure 2 is SEM photomicrographs of CAFB-8 stack fines illustrating variation in their physical characteristics. Some spherical particles were present that resembled cenospheres in typical coal ash. Larger particles were often agglomerates of finer particles. Figure 3 shows EDAX spectra of particles observed on SEM. An area scan by EDAX for the entire area shown on SEM in Figure 3(a) showed that the CAFB-8 stack fines consisted mostly of calcium. X-ray diffraction identified it to be CaO. Figures 3(b) and (c) show that even the submicron particles were high in calcium with minor elements such as sulfur, silicon, sodium, potassium, chlorine, iron, and zinc. Calcium oxide appeared to be the major component in all phases of the CAFB-8 stack fines, with the exception of the spherical particle shown in Figure 3(d), whose EDAX spectrum showed it to be mostly iron.

(a)



(b)

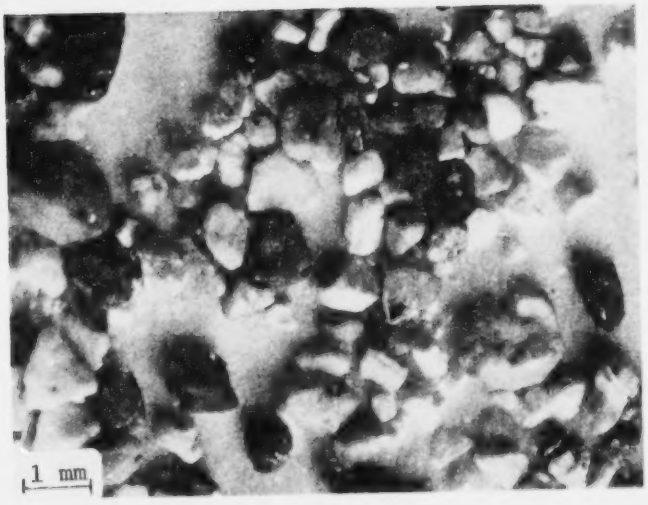


Figure 1 - Photomicrographs of (a) CAFB-8 Gasifier Material
(b) CAFB-8 Regenerator Material

Table 9

LEACHING RESULTS FROM THE CAFB-8 GASIFIER SPENT SORBENT

Leaching Conditions	Leachate Characteristics					
	pH	Sp. Cond., μmhos-cm^{-1}	Ca, mg/ℓ	Mg, mg/ℓ	$S^{=}$, mg/ℓ	$SO^{=}_4$ mg/ℓ
10 g, 100 ml, 48 hr, aerobic	12.3	8740	1384	9	-	300
10 g, 100 ml, 48 hr, anaerobic	12.3	8790	1256	31	1888	213
10 g, 100 ml, 100 hr, aerobic	12.2	10000	1780	31	704	745
10 g, 100 ml, 100 hr, anaerobic	12.0	13600	2400	31	2664	18
10 g, 100 ml, 240 hr, aerobic	12.1	11400	2596	12	448	2145
10 g, 100 ml, 240 hr, anaerobic	12.0	14800	2880	19	3392	25
10 g, 100 ml, 432 hr, aerobic	12.0	11250	2584	5	928	1272
10 g, 100 ml, 432 hr, anaerobic	11.8	15700	3440	5	2592	144

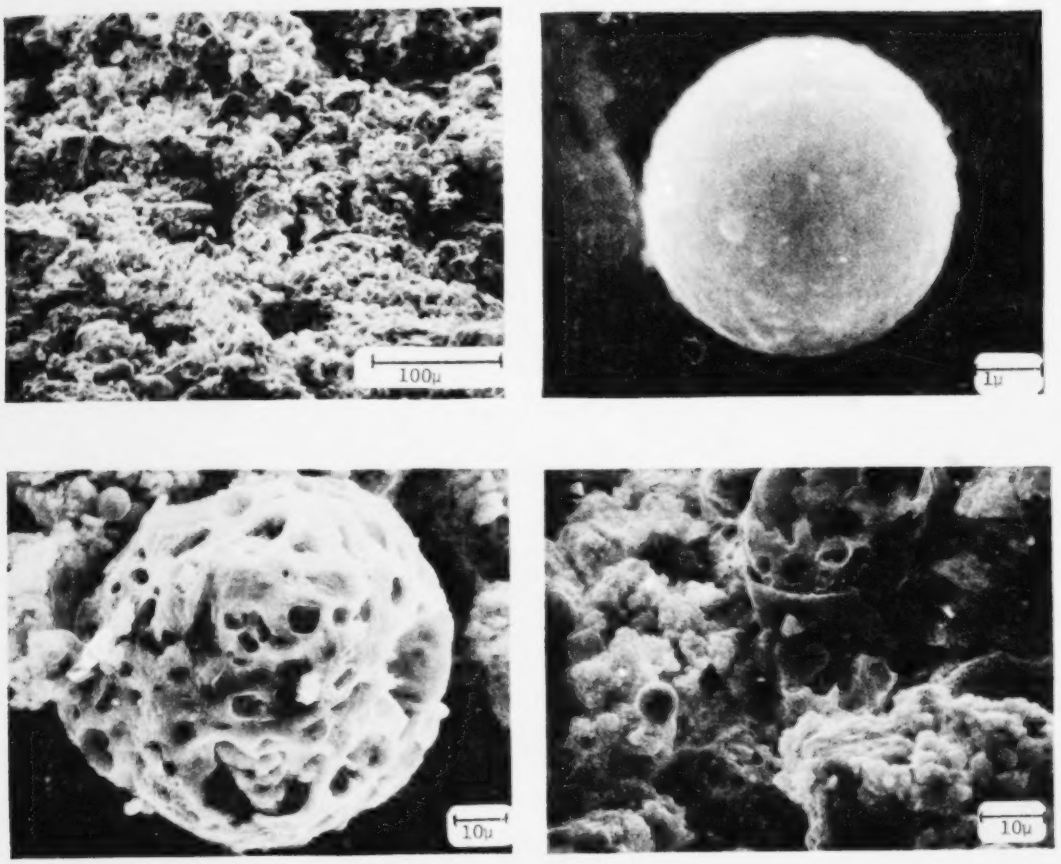


Figure 2 - SEM Photomicrographs of CAFB-8 Stack Fines Showing Variation of Their Physical Characteristics

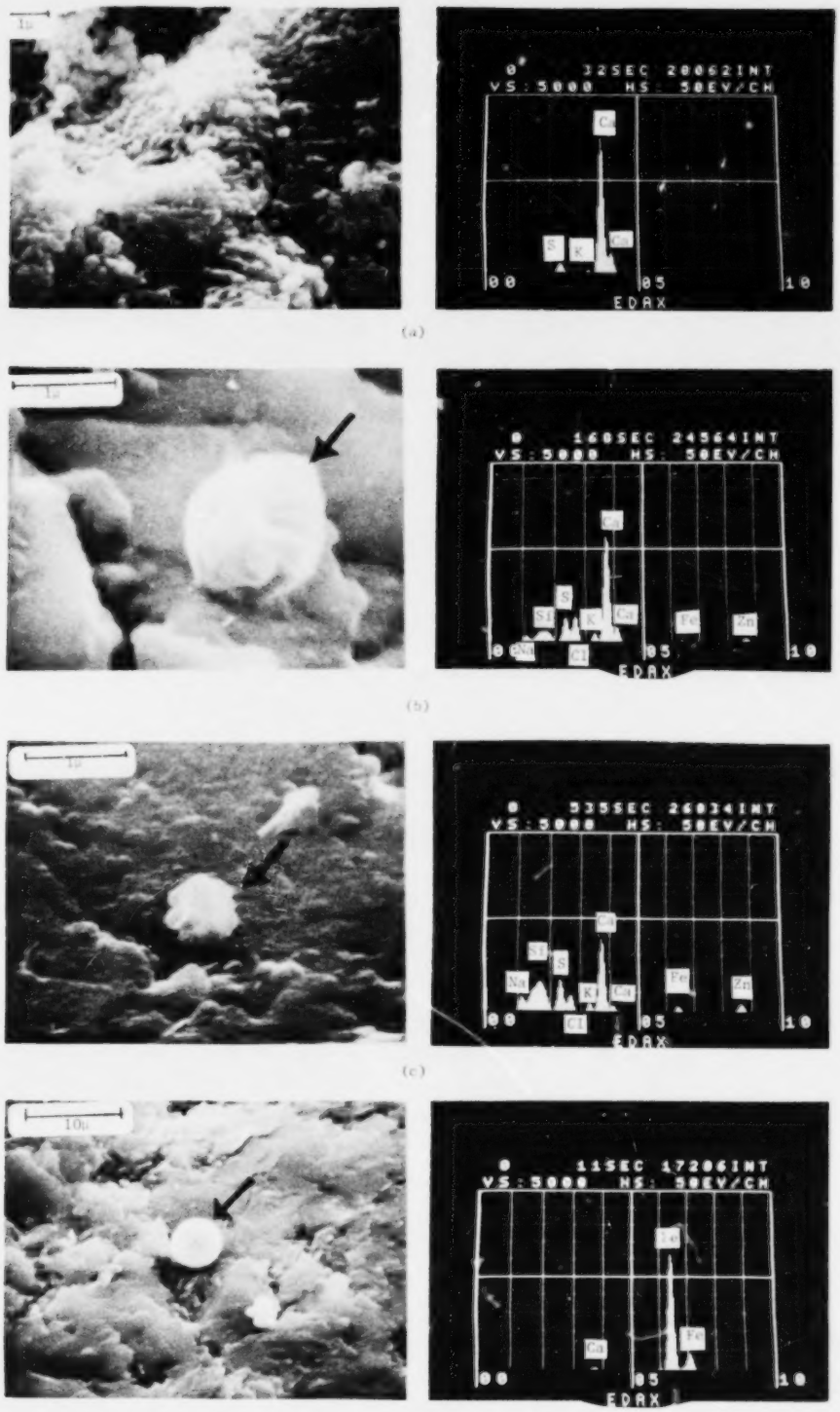


Figure 3 - SEM and EDAX of CAFB-8 Stack Fines

The amount of free carbon in the CAFB-8 stack fines was determined by TGA to be in the range of 5 to 8 percent by weight. Similar tests showed that the gasifier and regenerator bed materials from the same run contained less than 2 percent free carbon.

Standard leaching tests were conducted on CAFB-8 stack fines. Solid and leachate characteristics are summarized in Table 10. Note that the stack fines contain lower sulfide and higher sulfate than does the bed material, and the leachate of stack fines contains much less sulfide than does that from the bed material.

Trace metal element contents in the bed material and stack fines are compared for CAFB run 8. Results summarized in Table 11 indicate higher concentrations in the stack fines - for example, chromium, copper, mercury, manganese, sodium, lead, and vanadium. Table 11 also compares their leachates and indicates low dissolved trace elements in both.

The only element that did not meet the stringent DWS is mercury, whose concentration in the leachate of stack fines was 0.03 ppm as compared with the DWS for mercury of 0.002 ppm. This is not necessarily a problem because the amount of stack fines produced in a typical plant is relatively small compared with the total amount of spent solids from the bed.

CAFB-10, 10A Residue

CAFB-10 and 10A were runs in which mixed fuels were used (residual oil, bitumen, lignite, and coal). CAFB-10A from ERCA was run under the following conditions:

Sorbent	- Limestone BCR 1359
Average gasifier temp.	- 950°C
Average regenerator	- 1100°C
Run length	- 50 hr: 45 hr fuel oil
	5 hr coal - 1.5 hr Texas lignite
	3.5 hr Illinois No. 6

Table 10

CHEMICAL CHARACTERISTICS OF CAFB-8 STACK FINES AND LEACHATES

Sample	Leaching Conditions	Chemical Characteristics			
		Ca	Mg	$S^{=}$	SO_4
CAFB-8 Stack Fines	Solid	46.7 wt %	0.62 wt %	0.18 wt %	7.19 wt %
Leachate	10 g/100 ml/100 hr/aerobic	1504 mg/l	7.2 mg/l	-	1339 mg/l
Leachate	10 g/100 ml/100 hr/anaerobic	1440 mg/l	0	>100 mg/l	1116 mg/l
Leachate	10 g/100 ml/196 hr/aerobic	1624 mg/l	9.6 mg/l	< 20 mg/l	1094 mg/l
Leachate	10 g/100 ml/196 hr/anaerobic	1800 mg/l	9.6 mg/l	370 mg/l	1094 mg/l

Table 11

Dwg. 1689848

COMPARISON OF TRACE METAL ELEMENTS IN REGENERATOR BED MATERIAL AND STACK FINES OF CAFB-8

Substrate	Solid, ppm		Leachate, mg/ℓ		U. S. Drinking Water Standards.* mg/ℓ
	CAFB-8 Reg. Bed Mat'l	CAFB-8 Stack Fines	CAFB-8 Reg. Bed Mat'l	CAFB-8 Stack Fines	
Ag			<0.03	<0.01	0.05
Al			<1.0	0.02	
As			<0.003	<0.003	0.05
B			0.03	0.5	
Ba				<1.0	1.0
Be			≪0.1	<0.01	1.0
Bi	<1	<1	<0.03	<0.01	
Ca			>1000	Major	
Cd	<1	<1	<0.03	<0.01	0.01
Co	<3	<3	<0.1	<0.05	
Cr	5	10	<0.03	<0.05	0.05
Cu	2	5	0.08	<0.05	1.0
Fe			0.03	<0.1	0.3
Hg	0.03	4	<0.001	0.03	0.002
Mg			<1.0	<1.0	
Mn	50	100	<0.03	<0.05	0.05
Mo	3	3	0.08	0.2	
Na	50	>1000		>5.0	
Ni	1000	1000	<0.1	<0.05	2.0
Pb	10	30	<0.1	<0.05	0.05
Se			<0.003	<0.003	0.01
Si			0.2	0.3	
Sn			<0.1	<0.05	1.0
Sb			<0.1	<0.05	
Ti			<0.03	<0.05	
V	1%	2%	<0.03	<0.05	
Zn			<1.0	<1.0	5.0
Zr			<1.0	<0.05	

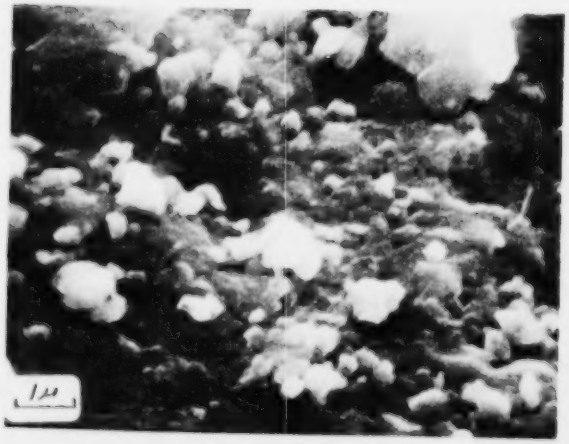
* DWS: NIPDWR 1976, USPHS 1962, and WHO, 1971

Figure 4 shows typical SEM photomicrographs and EDAX spectra of CAFB-10A gasifier material at the surface and fractured surface of a spent sorbent particle. EDAX spectra scanning the entire SEM area indicated the presence of silicon, aluminum, potassium, iron, and vanadium in addition to the major species calcium and sulfur. Higher sulfur is observed on the particle surface.

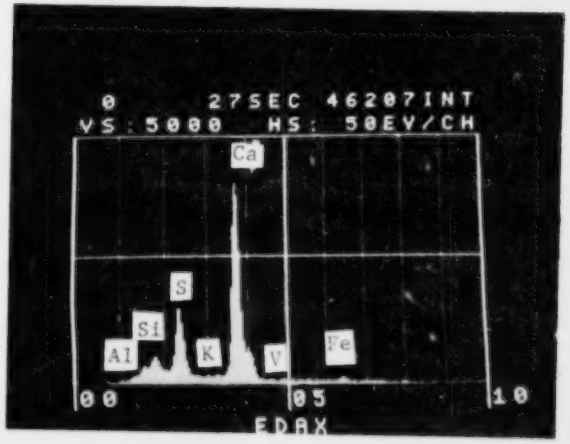
Electron microprobe analysis (EMA) provides elemental profiles of the particle cross-section. Figures 5 and 6 illustrate two types of sulfur profiles found in spent sorbent particles of the CAFB-10A gasifier sorbent. Figure 5(a) shows a photomicrograph of a cross-section of a partially sulfided limestone particle blocking the area scanned for calcium, sulfur, iron, silicon, and aluminum shown in Figures 5(b) to (f). The concentration of an element is proportional to the intensity of the X-ray counts. Calcium is evenly distributed, and sulfur concentrates on the particle periphery, as do iron and silicon in this case. Figure 6 shows an opposite sulfur gradient with sulfur depletion at the particle surface. We suspect that this type of particle is formed during regeneration when a fully sulfided limestone particle is partially regenerated to CaO, which is more concentrated at the surface of the particle. A third type of sulfur configuration, not shown in these figures, has sulfur evenly distributed throughout the particle.

Table 12 summarizes the leaching results and indicates the following:

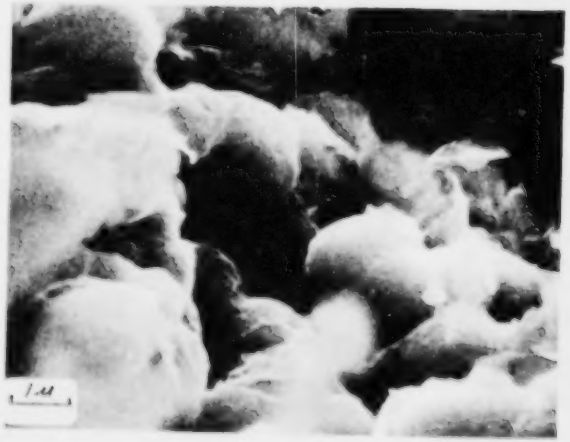
- Leachates are high in pH and TDS attributable to CaO present as a major species in the solid.
- Sulfide in the leachate is lower than the previously tested CAFB spent sorbents as is consistent with the lower sulfide content present in the CAFB-10A gasifier solid.
- Sulfate in leachate is dominated by the $CaSO_4$ present in the solid, which is higher in CAFB-10A spent sorbent than in the previously tested CAFB spent stones.



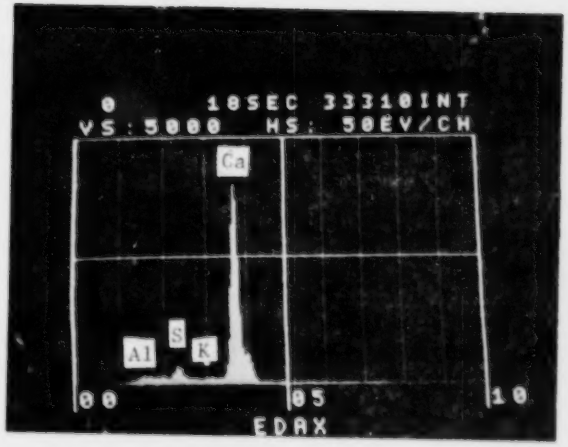
(a)



(b)



(c)



(d)

Figure 4 - SEM and EDAX of CAFB-10A Gasifier Bed Material
(a) (b) particle surface
(c) (d) fractured surface

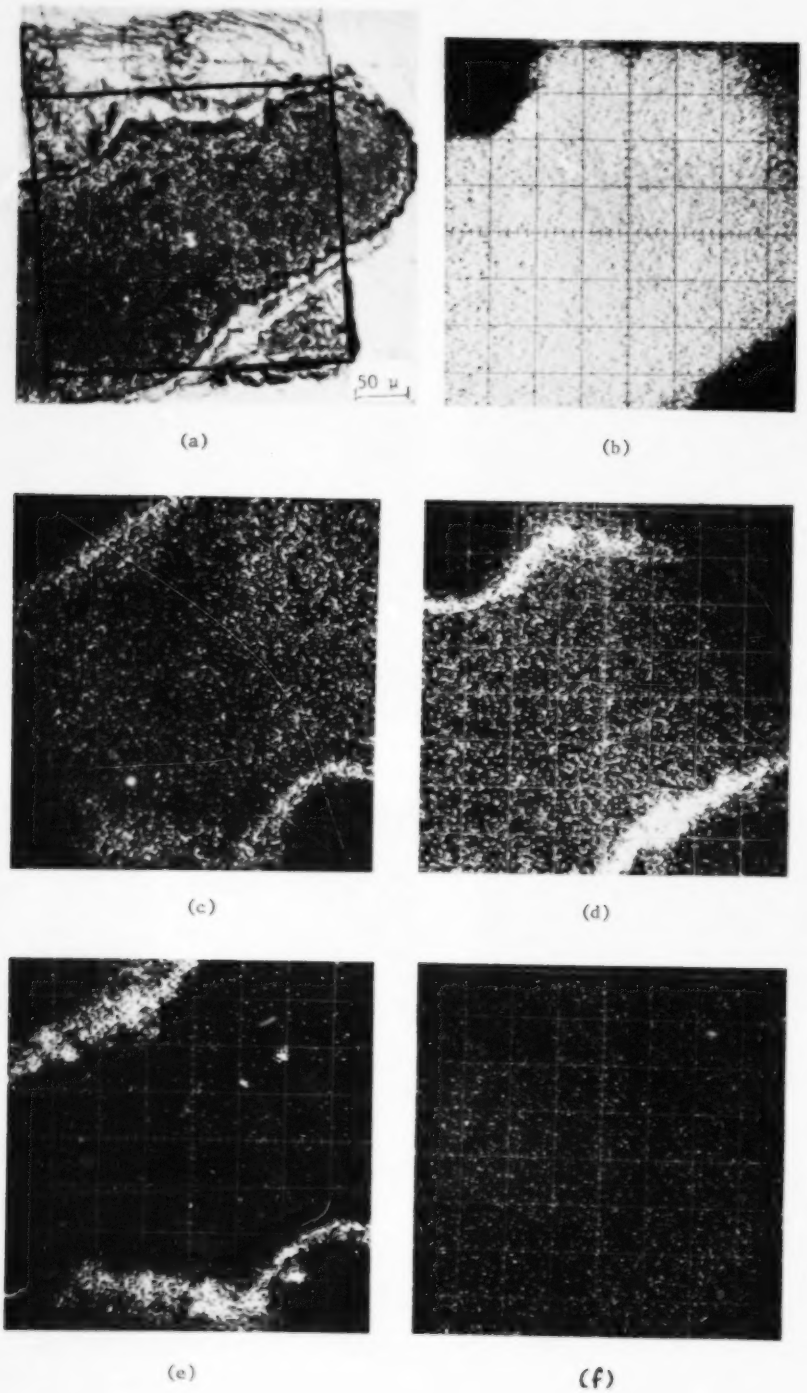


Figure 5 - (a) Photomicrograph of a Cross Section of a Spent CAFB-10A Gasifier Sorbent Particle Blocking the Area for Electron Microprobe Analysis
(b) EMA Area Scan for Ca, (c) for S, (d) Fe, (e) Si, (f) Al

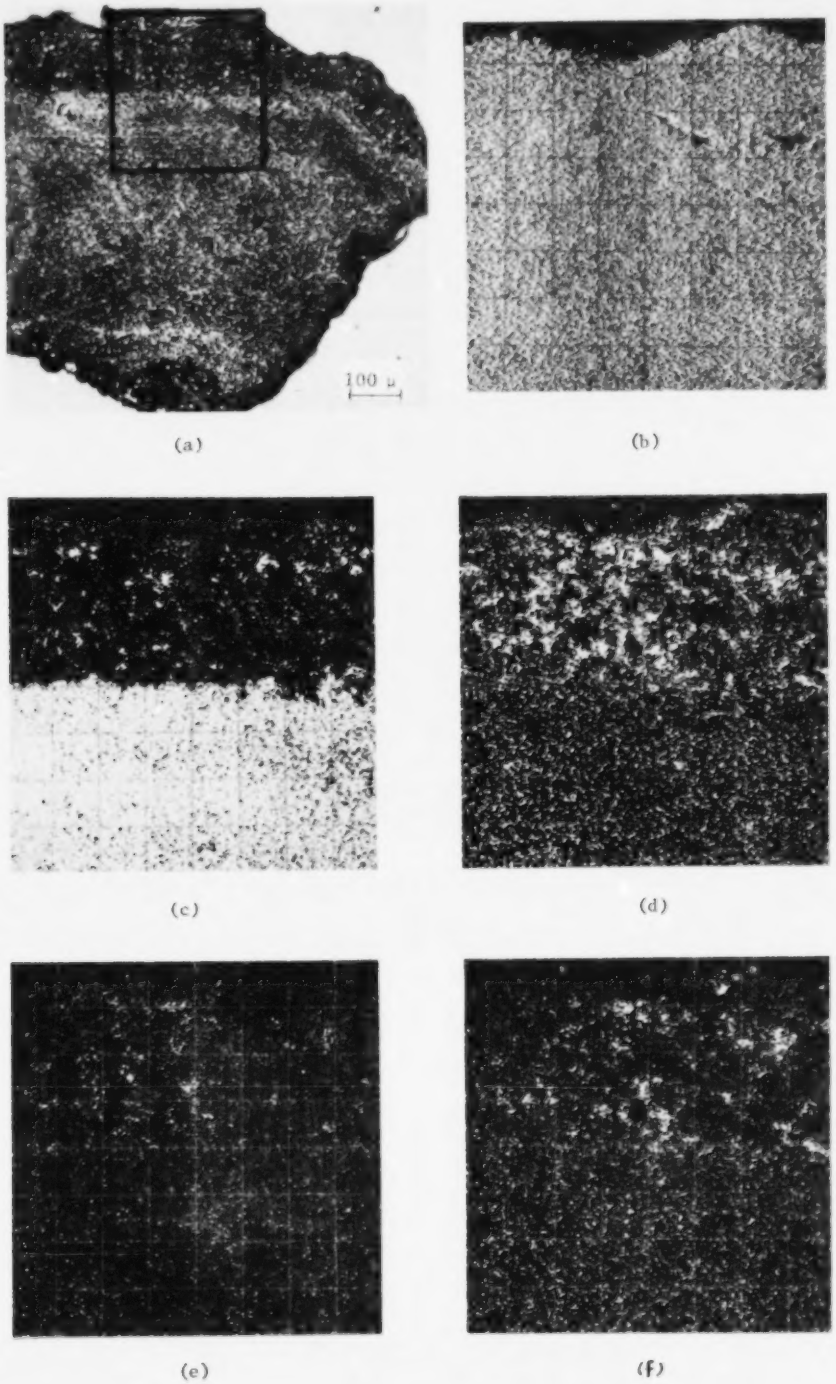


Figure 6 - (a) Photomicrograph of a Cross Section of a Spent CAFB-10A Gasifier Spent Sorbent Particle Blocking the Area for EMA Scan
(b) EMA Area Scan for Ca, (c) S, (d) Fe, (e) Si, (f) Al

Table 12

CHEMICAL CHARACTERISTICS OF CAFB-10A GASIFIER MATERIAL AND ITS LEACHATES

Dwg. 1704832

Samples	Leaching Conditions	Chemical Characteristics							
		pH	Specific Conductance, μmhos/cm	Ca	Mg	$S^{=}$	$SO_4^{=}$	$CO_3^{=}$	OH^{-}
CAFB - 10A Gasifier Stone, wt %	Before leaching	-		57.6	0.83	0.78	9.62	0.8	0.17
	After leaching 10/g/100 ml/100 hr/aerobic	-		*	*	*	*	21	5.1
Leachates, mg/ℓ	10 g/100 ml/100 hr/aerobic	12.2	11130	1708	< 10	*	1263	*	*
	10 g/100 ml/100 hr/anaerobic	12.2	11230	1768	< 10	150	1311	*	*
	10 g/100 ml/196 hr/aerobic	12.3	11740	1572	< 10	91	1395	*	*
	10 g/100 ml/196 hr/anaerobic	12.3	8620	1472	< 10	374	1139	*	*

* Not determined

- The leached stones contain much more $Ca(OH)_2$ and $CaCO_3$ than does the original stone due to the hydration and carbonation of CaO during the leaching process.

In order to correlate the various EPA contractors' efforts in the area of CAFB spent sorbent disposal, samples were requested and received from the Ralph Stone Company.[39] These included five batches of Exxon and PER spent sorbent and fly ash from the FBC process[33,34,40] and two CAFB spent solids from the ERCA pilot unit.

Leaching studies were carried out on the CAFB spent materials. Two methods were employed: the continuous leach test reported previously and an intermittent leach test.

Figure 7 shows results from the continuous leaching. Two points are noted. First, calcium and sulfide increase with mixing time, indicating that CaS equilibrium between the solid and aqueous phase is not achieved in 200 hours. Secondly, the CAFB-10A bed and CAFB-10 gasifier fly ash display similar leachate characteristics except that higher dissolved sulfide is found in the leachate of the bed material, consistent with the solid analysis.

Results from the intermittent shaker tests of several CAFB residues are shown in Figure 8. Several points can be noted:

- All leachates had similar pH and sulfate that improved only very slightly with total leachate volume and time.
- The repeatability of the two batches of CAFB-10A was good (CAFB-10A and RS-CAFB-10A).
- CAFB-8 regenerator material, which had higher sulfide content in the solid, produced leachate with higher $S^=$, Ca, and TDS, as would be expected from the greater CaS dissolution.
- Initial TDS was worst for CAFB-8 regenerator sorbent and best for CAFB-10 fly ash. All converge to a similar value after several 72-hour intervals.

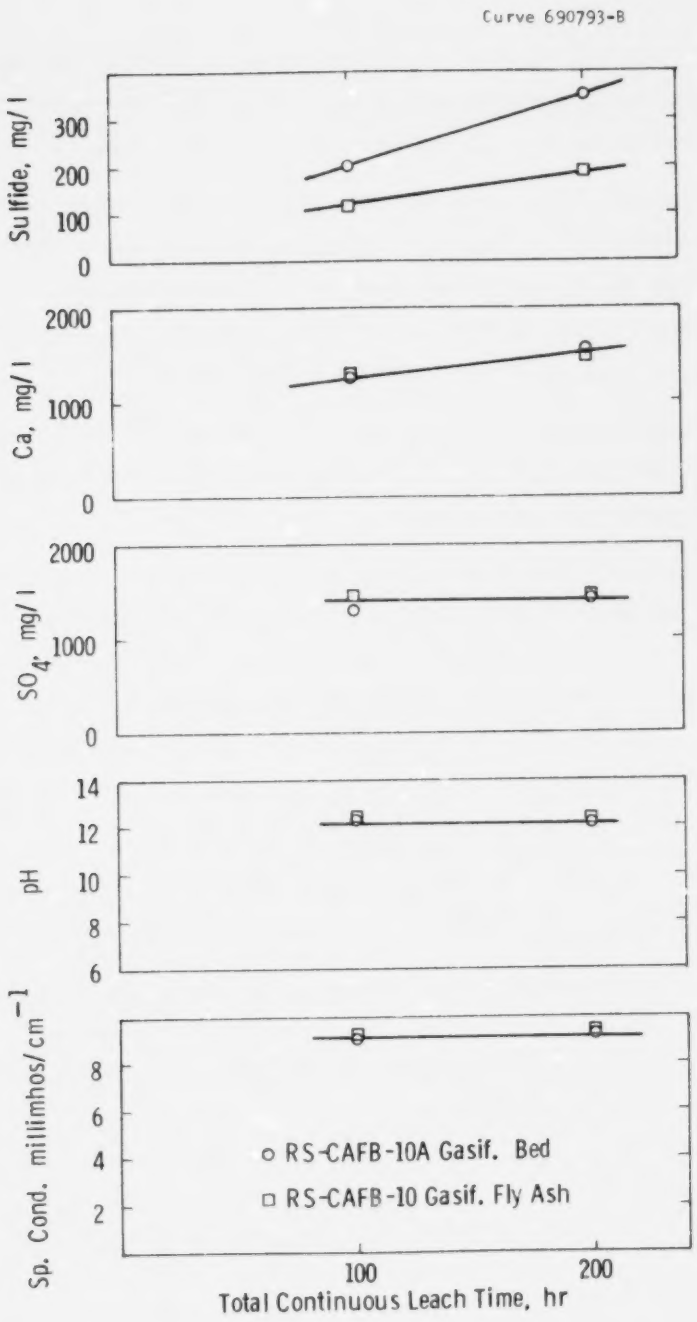


Figure 7 - Leachate Characteristics as a Function of Total Continuous Leach Time for the CAFB Samples Obtained via the Ralph Stone Co.

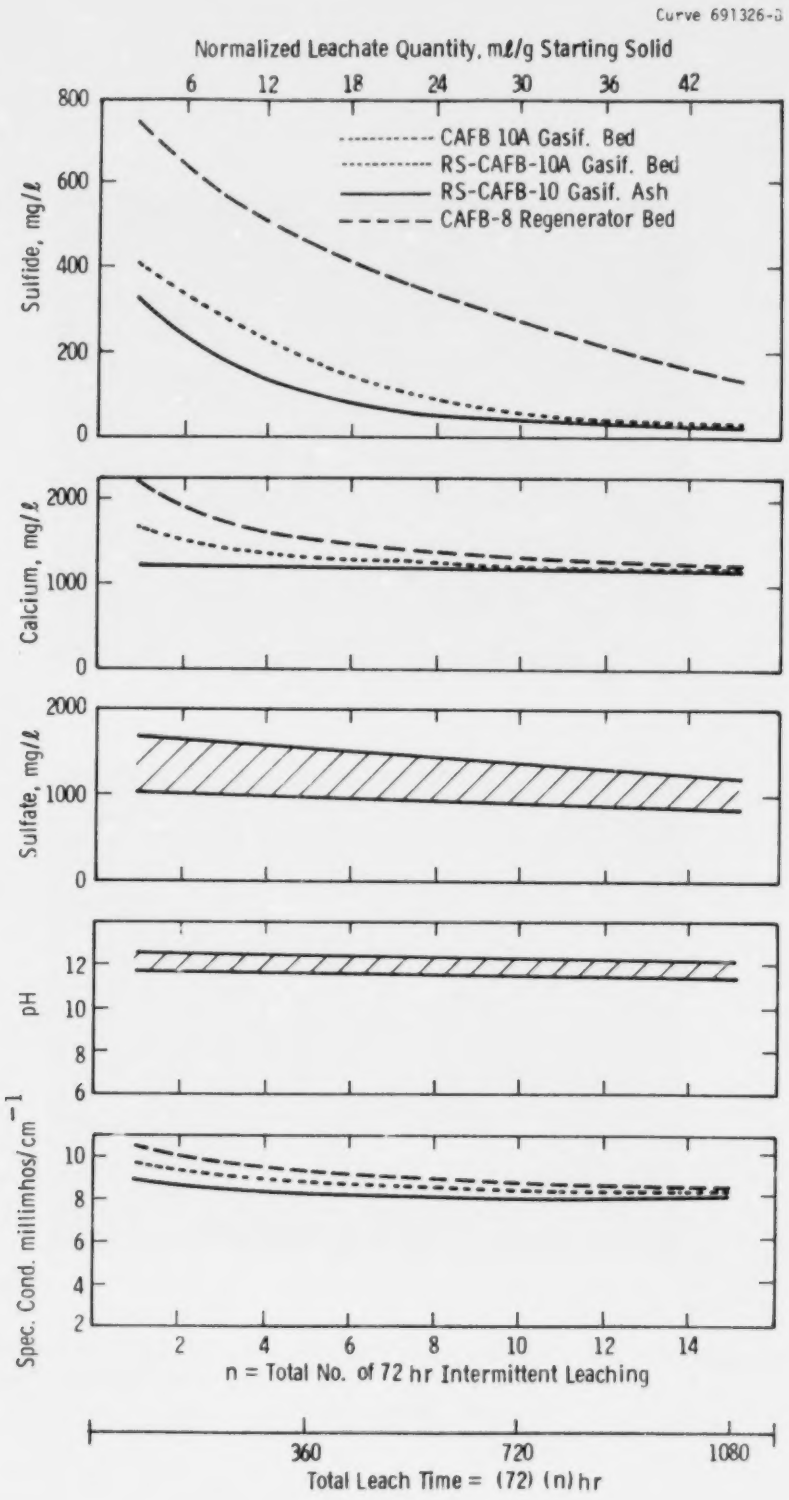
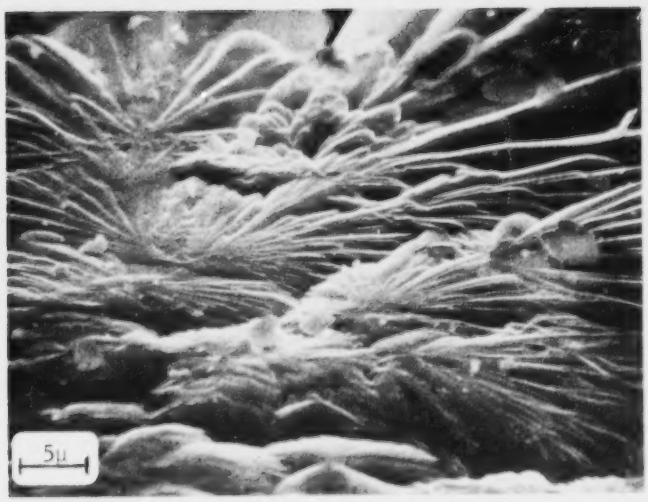
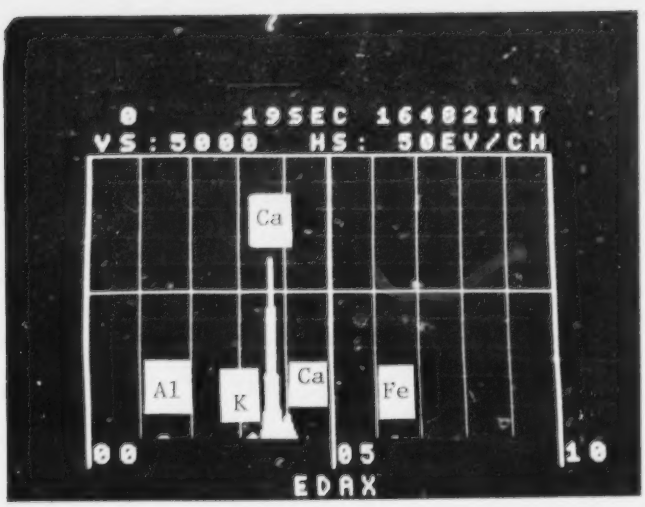


Figure 8 - Leachate Characteristics as a Function of Intermittent Leaching for the CAFB Samples



(a)



(b)

Figure 9 - (a) SEM Photomicrograph and (b) EDAX Spectrum of the White Precipitate Formed Readily in Air from the Leachate

- CAFB spent solids tested so far contained high concentrations of CaO, and their leachate did not seem to improve considerably with time.

White crystalline precipitate found on the leachate surface when the leachate was stored overnight has been identified by X-ray diffraction and by TGA to be $CaCO_3$ (calcite) that must have been formed by carbonation of dissolved calcium with carbon dioxide (CO_2) in air. Figure 9 shows a SEM and EDAX of such precipitate. Trace metal elements were determined on these solids and their leachates. Results from the CAFB spent materials which are presented in Table 13 show that the trace metal element content in these leachates is below the U. S. drinking water standards. This is consistent with our previous report based on analyses of other batches of spent sorbent from the CAFB process.

CAFB-11 Residue

CAFB-11 was a 100 hr run using Texas lignite, during which GCA[41] carried out the Level I environmental sampling.[26] The operating conditions are summarized in Table 14. Four types of samples collected by GCA personnel during the run were tested for the environmental impact of disposal.

The gasifier and regenerator bed materials were granular, similar to the previously tested spent sorbents from residual oil runs. Figure 10 shows microphotographs of a cross-section of a spent sorbent particle from the regenerator and elemental profiles (Ca, Mg, S, Si, Al, Fe, and C) on an area near the surface. Calcium is evenly distributed in the calcium-based sorbent particle. Sulfur, silicon, aluminum, and iron are more concentrated on the particle periphery, suggesting an ash deposit at the particle surface of approximately 10 μm thickness. Carbon, however, is depleted at the particle surface where ash coating exists. The gasifier and the regenerator residues appear to be very similar.

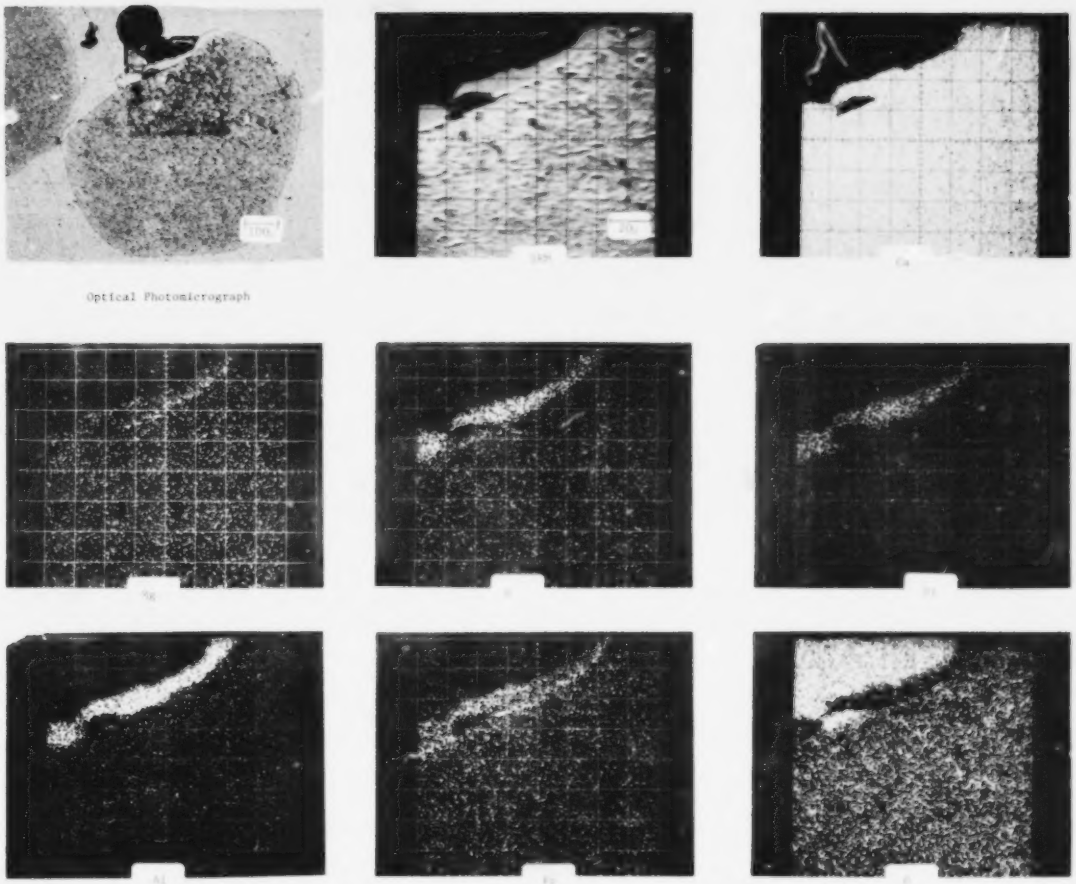


Figure 10 - Electron Microprobe Analysis of Spent Regenerator Bed Material from CAFB "Lignite" Run

Table 13

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TRACE METAL CONTENT IN THE CAFB SPENT SORBENTS OBTAINED THROUGH RALPH STONE CO. AND THEIR LEACHATES

Substance	Solid (w%)		Leachate (mg/ℓ)		U. S. Drinking Water Standards. mg/ℓ
	RS-CAFB 10A Gasif. Bed	RS-CAFB-10 Gasif. Fly Ash	RS-CAFB 10A Gasif. Bed	RS-CAFB-10 Gasif. Fly Ash	
Ag			<0.01	<0.01	0.05
Al	>10	3	0.05	0.05	
As	<0.003	<0.003	0.003	0.003	0.05
B	0.01	0.001	0.8	0.5	
Ba			<1.0	<1.0	1.0
Be	0.0001	<0.0001	<0.01	<0.01	1.0
Bi	<0.0003	<0.0003	<0.01	<0.01	
Ca	>>10	>>10	Major	Major	
Cd	<0.003	<0.003	<0.01	<0.01	0.01
Co	<0.0005	<0.0005	<0.05	<0.05	
Cr	0.003	0.003	<0.05	<0.05	0.05
Cu	0.005	0.003	<0.05	<0.05	1.0
Fe	>10	3	<0.1	<0.1	0.3
Hg			<0.001	<0.001	0.002
Mg	1.0	0.3	<1.0	<1.0	
Mn	0.005	0.005	<0.05	<0.05	0.05
Mo	0.001	0.001	0.1	0.1	
Na	<0.03	<0.03	<5.0	>5.0	
Ni	0.01	0.03	<0.05	<0.05	2.0
Pb	<0.001	0.001	<0.05	<0.05	0.05
Sb			<0.05	<0.05	
Se			0.003	<0.003	0.01
Si	>10	>10	5.0	5.0	
Sn	0.0003	<0.0003	<0.05	<0.05	1.0
Sr			>5.0	>5.0	
Ti	0.02	0.02	<0.05	<0.05	
V	0.03	0.3	<0.05	<0.05	
Zn	<0.01	<0.01	<1.0	<1.0	5.0
Zr	<0.01	<0.01	<0.1	<0.1	

Table 14

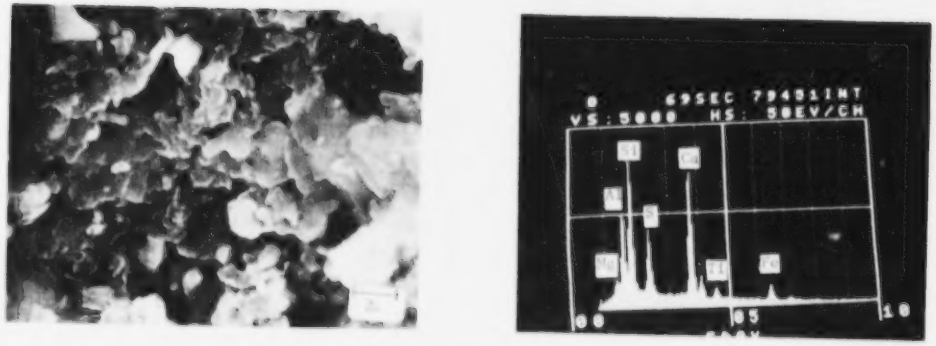
CAFB-11 OPERATING CONDITIONS

Average Coal Feed Rate	211 kg (465 lb)/hr	
Average Line Feed Rate	10.4 kg (23 lb)/hr	Measured
Air to Gasifier	3682-4184 dm^3 (130-170 df)/min	
Air to Regenerator	595-736 dm^3 (21-26 cf)/min	
Temp. in Regenerator	Set at 1055°C	by
Regenerator Bed Depth	61-127 cm (24-50 in)	
Gasifier Bed Depth	56-61 cm (22-24 in)	
Regenerator Drain	Set at 113 dm^3 (4 cf)/hr	ERCA
Regenerator SO_2	0-1.2%	Measured
Regenerator CO_2	5-17%	by
Regenerator O_2	0.2-5%	ERCA
Stack SO_2	173 ppm - GCA	
	260 ppm - Avg. for day	
	by ERCA	

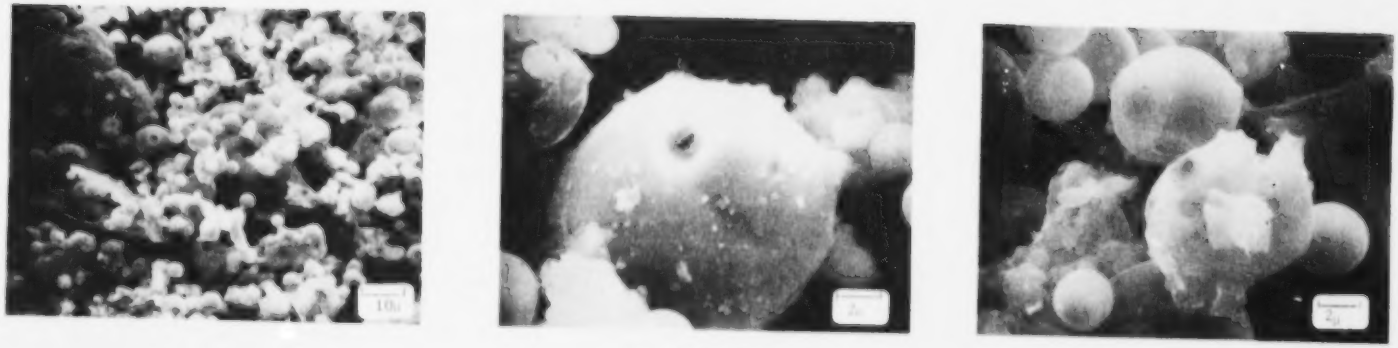
The residue from the main cyclone consisted of finer granular sorbent particles, ash, and carbon. The ash content (Si, Al) in the CAFB-11 cyclone carry-overs was much higher than the cyclone ash from the oil gasification runs. Figure 11 shows SEM and EDAX of the main cyclone and stack cyclone fines. Unlike the main cyclone ash, the stack fines from the Texas lignite run consisted of mixtures of sorbent fines and cenospheres. The latter were not seen in the oil gasification residues. The SEM and EDAX of these are shown again in Figure 12, where chemical and physical characteristics are correlated for various particles. In general, the spent sorbent fines are of irregular shape and are predominantly calcium. The very bright, nonspherical particles are SiO_2 (quartz). The cenospheres were high in silicon and aluminum.

The chemical compositions and leaching properties of CAFB-11 residues were determined. The results are shown in Tables 15 and 16. The following points are worth noting:

- The gasifier and the regenerator materials appear to be similar not only in physical characteristics but also in chemical composition. Therefore, leaching tests were carried out only on the regenerator material.
- The carry-over materials contained a much smaller amount of sorbent fines than did the carry-over from the oil gasification runs. Thus, calcium and TDS were also lower in the leachate of CAFB-11 carry-over.
- Sulfur content (both $S^=$ and $SO_4^=$) was low in the residues from the lignite run, due to the low sulfur content in Texas lignite.
- Trace elements were more concentrated in the carry-over and were highest in the stack fines (B, Ba, Cr, Cu, Mn, Mo, Ni, Pb, Sr, Ti, Zr).
- Leachate from CAFB-11 bed material was similar to the leachate from the oil gasification residues except for the lower $S^=$ and $SO_4^=$ concentrations in the former.



Main Cyclone



Stack Cyclone

Figure 11 - SEM and EDAX of Stack Cyclone Fines from CAFB "Lignite" Run Material

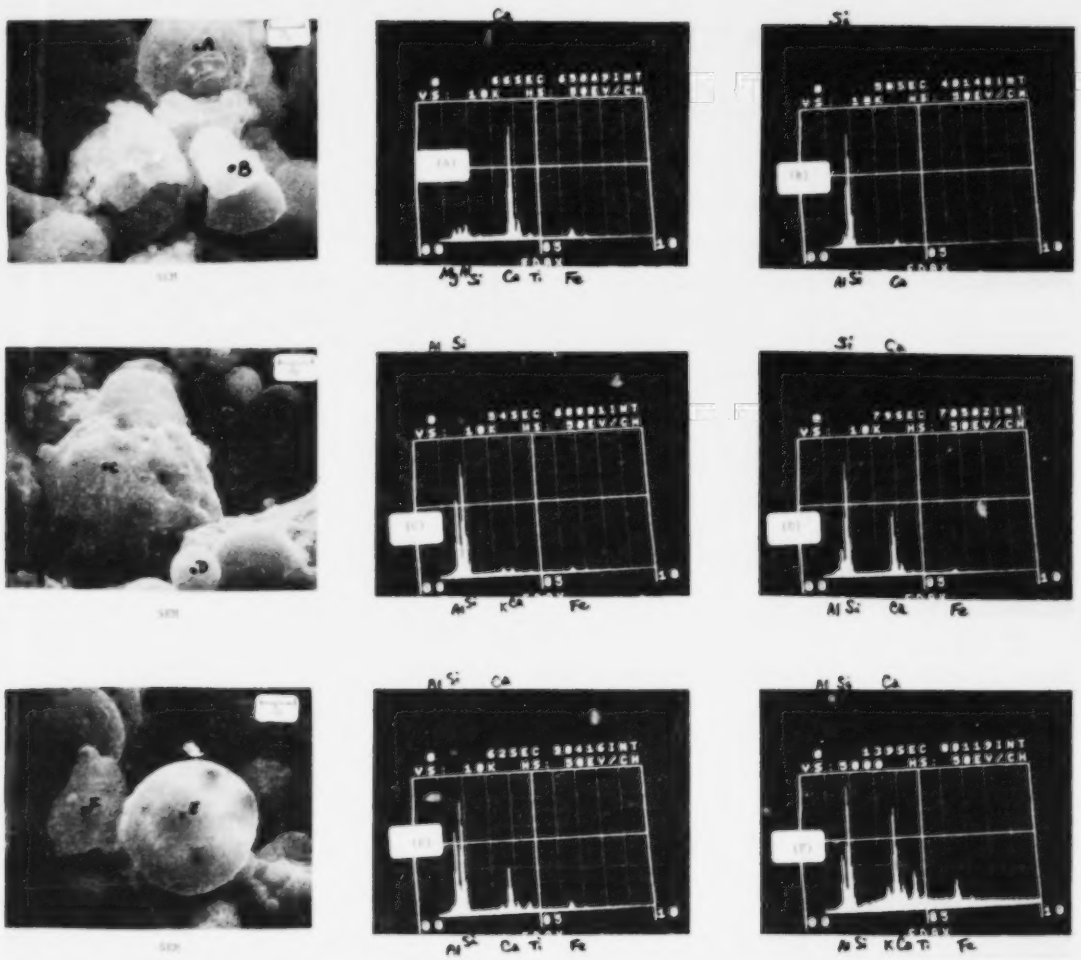


Figure 12 - SEM and EDAX of Stack Cyclone Fines
from CAFB "Lignite" Run

Table 15

SOLID AND LEACHATE CHARACTERISTICS OF SPENT MATERIAL FROM CAFB "LIGNITE" RUN

	Solid, wt %				Leachate, mg/ℓ						
	Ca	Mg	$S^{=}$	SO_4	pH	S.C., μmhos/cm	Ca	Mg	$S^{=}$	SO_4	
Gasifier Bed	49.6	0.8	0.22	0.1							
Regenerator Bed	52.1	0.3	0.1	0.97	11.7 11.7	7690 8250	812 888	<10 <10	37 100	206 200	Aerobic Anaerobic
Main Cyclone	6.4	0.5	0.2	0.2	11.1 11.4	1330 2400	152 204	<10 <10	38 56	77 38	Aerobic Anaerobic
Stack Cyclone	8.7	1.3	0.13	2.7	10.3 10.9	1150 1310	240 232	<10 <10		544 343	Aerobic Anaerobic

Dwg. 2618C99

Table 16

CHEMICAL CHARACTERISTICS OF CAFB "LIGNITE" RUN RESIDUES AND LEACHATES

Substance	(a) Solid, ppm			(b) Leachate, mg/ℓ						(c) DWS, mg/ℓ
	(1)	(2)	(3)	(1) Ae	(1) An	(2) Ae	(2) An	(3) Ae	(3) An	
Al	Major	Major	Major	< 1	< 1	> 1	> 1	< 1	< 1	
Ag	< 1	< 1	< 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
As				< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.05
B	300	300	1000	2	2	1	1	1	1	
Ba	100	500	1000	< 1	< 1	< 1	< 1	< 1	< 1	1.0
Be	1	1	< 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Bi	< 1	< 1	< 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Ca	52.1%	6.4%	8.7%	812	888	152	204	240	232	200
Cd	< 3	< 3	< 3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Co	10	10	< 10	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	
Cr	50	100	100	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.05
Cu	5	10	10	< 1	< 1	< 1	< 1	< 1	< 1	1.0
Fe	Major	Major	Major	< 0.2	< 0.2	1	< 0.2	> 1	< 0.2	0.3
Hg				< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Mg	0.3%	0.5%	1.3%	< 10	< 10	< 10	< 10	< 10	< 10	150
Mn	200	500	1000	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
Mo	< 10	< 10	10	0.06	< 0.06	0.2	0.06	0.3	< 0.05	
Na	1000	1000	1000	2	2	> 1	> 1	> 1	1	
Ni	10	20	30	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	2.0
Pb	< 10	30	50	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.05
Sb	< 50	< 50	< 50	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
Se				< 0.01	< 0.01	< 0.01	< 0.01		0.15	0.01
Si	Major	Major	Major	0.6	1	> 1	> 1	> 1	> 1	
Sn	< 10	< 10	< 10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.0
Sr	500	1000	> 1000	> 1	> 1	> 1	> 1	> 1	> 1	
Ti	> 1000	> 1000	>> 1000	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
V	> 1000	300	1000	< 0.05	< 0.05	< 0.02	< 0.05	< 0.09	< 0.05	
Zn				< 4	< 4	< 4	< 4	< 4	< 4	5.0
Zr	100	1000	1000	< 1	< 1	< 1	< 1	< 1	< 1	
SO_3				< 10	< 10	< 10	< 10	< 10	< 10	
$S^=$	0.1%	0.2%	0.13%	37	100	38	56			
SO_4	0.97%	0.13%	2.7%	206	200	77	38	544	343	250
F				1.6	1.9	7.9	8.4	2.4	2.7	2.4
Cl				11	12	11	13	23	72	250
Br				< 1	< 1	< 1	< 1	1.8	< 1	
NO_2				< 1	< 1	< 1	< 1	20	22	
NO_3 (as N)				< 1	2	< 1	2.5	7	12	10
PO_4				< 1	< 1	< 1	< 1	< 1	< 1	
Free C	< 1%	~ 27%	~ 3%							
TOC				< 20	< 20	< 20	< 20	< 20	< 20	
pH				11.7	11.7	11.1	11.4	10.3	10.9	5 to 9.0
SC, μmhos/cm				7690	8250	1330	2400	1150	1310	~ 750

(a) (1) Regenerator Bed Material
(2) Main Cyclone Material
(3) Stack Cyclone Material

(b) Ae Aerobic Conditions
An Anaerobic Condition

(c) DWS NIPDWR, USPHS, and WHO Drinking Water Standards
▨ Exceed DWS

- The anaerobic leachate contained higher Ca, $S^{=}$, and TDS, in general, than did the aerobic.
- DWS were met by the bed leachate but exceeded (Fe, F, Se) by the leachate from the carry-over. Leachate from TUGCO ash (a Texas lignite ash from a conventional boiler) also exceeded the DWS for Cr and Se, as will be discussed in a later section.
- Like the oil gasification residue, Ca, SO_4, pH, and TDS were major concerns for the leachate.

Note that CAFB-11 was the only residue from the Texas lignite test at the time of this work. The residues, thus, may not be representative because of the unstable conditions existing during at least part of the test duration.

The heat-release property of CAFB-11 summarized in Table 17 falls within the range found for the residues from the oil run, which will be discussed in a later section.

Processed Residue

Dry Sulfation

The dry sulfation (DS) scheme is designed to sulfate the spent regenerator material (CaO, CaS) with the SO_2 from the regenerator off-gas.[3,9,12]

Four samples that were sulfated to various degrees were investigated in this category. Table 18 summarizes the samples and their sulfate and sulfide contents. The leachate characteristics were determined as functions of stone load and mixing time. Figures 13 and 14 present leaching results of the DS mix and compare them with CAFB-7 regenerator stone before sulfation. Since the sulfated product is largely $CaSO_4$, leaching results of a natural gypsum (Iowa Gypsum No. 114) are also presented for comparison. From Figures 13 and 14 one could make the following points:

- Sulfide in the leachate was drastically reduced by the dry-sulfation processing of the CAFB regenerator stone.

Table 17

RESIDUAL ACTIVITY OF SPENT CAFB "LIGNITE"
RUN MATERIAL BY HEAT-RELEASE

Sample Source	Max. Temp. Rise	
	3g/20 mℓ	8g/2 mℓ
Gasifier Bed	20°C (10 min)	163°C (3 min)
Regenerator Bed	17.5°C (10 min)	133°C (3 min)
Main Cyclone	1.3°C (3 min)	16°C (10 min)
Stack Cyclone	<0.2°C	<0.2°C

Table 18

SULFUR CONTENTS IN CAFB-9 SPENT SORBENT AND
DRY-SULFATED CAFB-9 SPENT SORBENT

Spent Sorbents	Processing History	Sulfate, wt %	Sulfide, wt %
CAFB-9	Actual spent sorbent from the regenerator bed of ERCA's pilot plant	3.07	2.24
CAFB-903	∿50 m % sulfated CAFB-9 in the 10-cm fluidized-bed laboratory unit	40.2	0.59
CAFB-904	79 m % sulfated CAFB-9 (44 to 420 μm)	65.2	0.16
CAFB-904 (125-177 μm fraction)	94 m % sulfated CAFB-9 (125 to 177 μm)	68.8	0.1

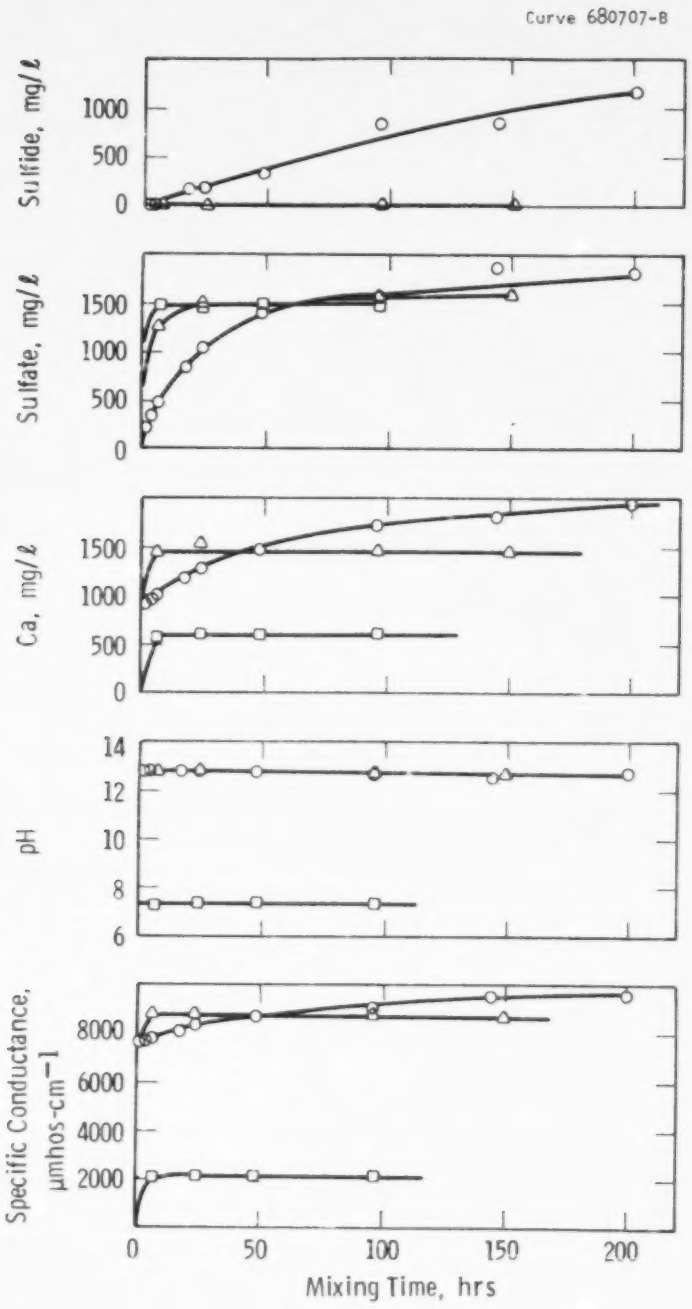


Figure 13 - Leachate Characteristics as Functions of Batch Mixing Time for:
- o CAFB Regenerator Stone No. 7
- Δ 76 m% CAFB-7 - DS mix
- □ Iowa Gypsum No. 114

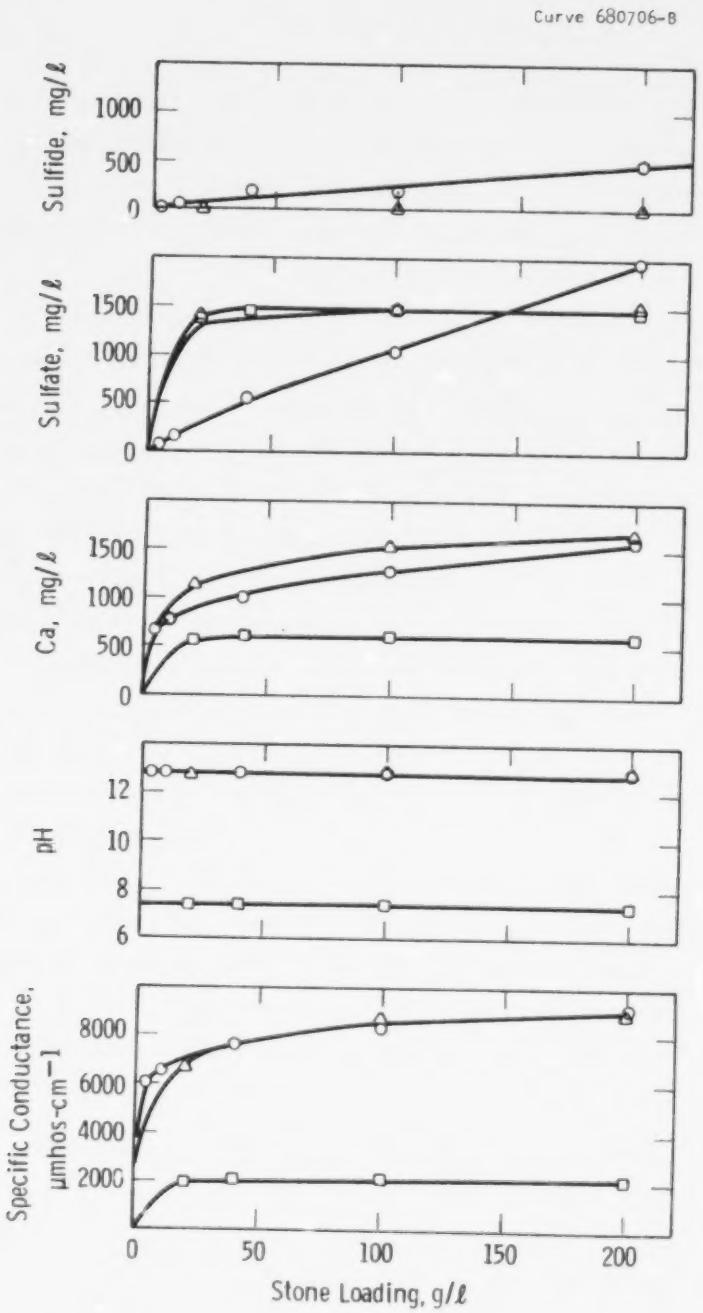


Figure 14 - Leachate Characteristics as a Function of Stone Loading for:
- o CAFB Regenerator No. 7
- Δ 76 m% CAFB-7 - DS mix
- □ Iowa Gypsum No. 114

- Sulfate concentrations in both the CAFB regenerator stone and the sulfated DS mix exceeded the DWS (250 mg/ℓ). Leachates from a natural gypsum, however, contained similarly high dissolved sulfate, which was consistent with the saturated $CaSO_4$ solution.
- Gypsum leachates had lower pH, calcium, and total dissolved ions than did the 76 m % CAFB spent stone.

Spent sorbent CAFB-9 was sulfated to various degrees (CAFB-903, CAFB-904). The sulfated CAFB-904 was further sieved to separate the fraction of smaller particle size (125-177 μm which achieved a 94 m % sulfation.[3,9,12] Leaching tests were conducted separately on these differently sulfated spent sorbents. A general trend was noted - leachate calcium, sulfide, TDS, and pH decreased with an increasing degree of sulfation. Figure 15 compares leachate sulfide for aerobic and anaerobic cases and shows that sulfide concentration was much less under aerobic conditions. It also shows that the sulfide in the leachate was significantly reduced by the degree of sulfation. Similar plots are shown in Figure 16 for specific conductance which are a good approximation for TDS: 1.5 μmhos-cm^{-1} is approximately equivalent to 1000 mg/ℓ. TDS are lower under aerobic leaching and decrease with increasing sulfation. Leachate pH is high for unsulfated and partially sulfated spent sorbent but falls within the water quality criteria range for the 94 m % sulfated sample. Trace metal contents were also determined and indicated little of concern.

In summary, the leaching results of the sulfated spent sorbent demonstrated that the leachate quality is significantly improved by "dry sulfation" processing of the spent sorbents from the CAFB gasification process so that the potential water pollution would be greatly reduced.

Dead-Burning

Processing by dead-burning aims to deactivate the CaO activity by high-temperature sintering.

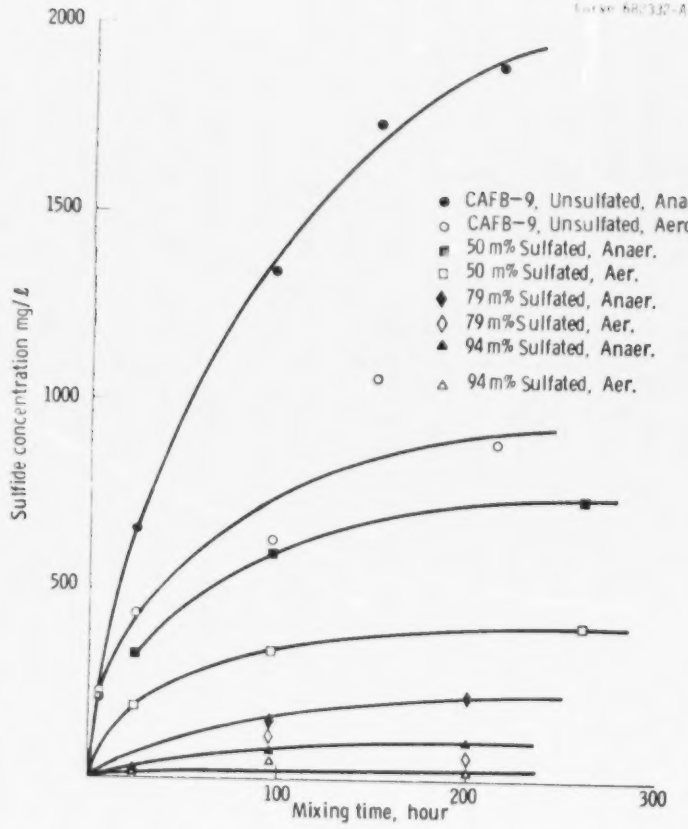


Figure 15 - Comparison of Dissolved Sulfide in Leachates of Sulfated and Unsulfated CAFB-9 Spent Sorbent

Curve 682331-A

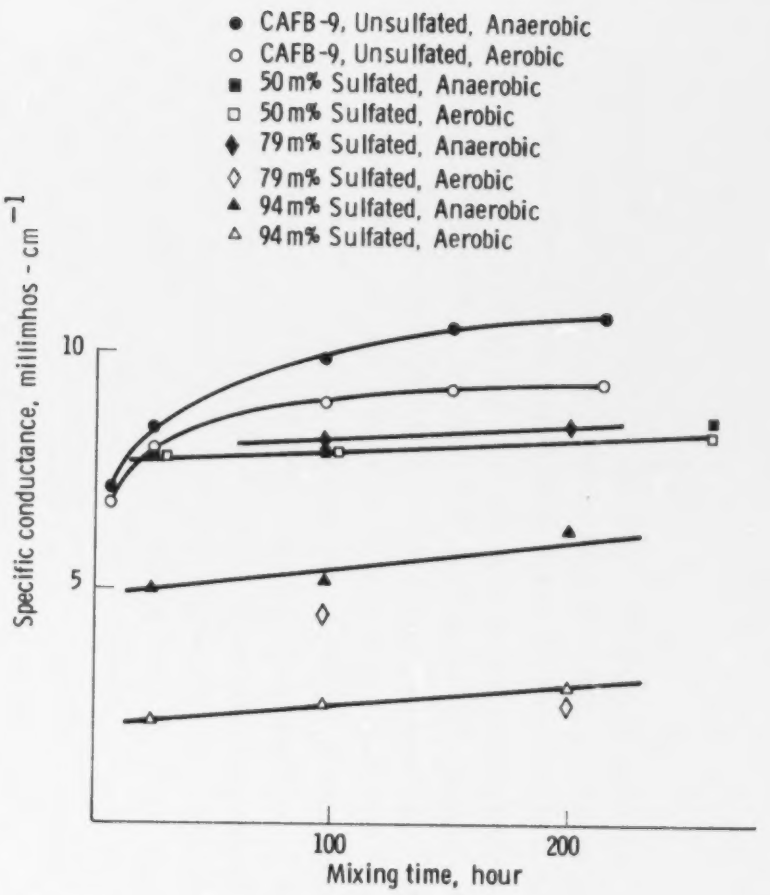


Figure 16 - Comparison of Specific Conductance of Leachates of Sulfated and Unsulfated CAFB-9 Spent Sorbent

Leaching studies were carried out on numerous dead-burned CAFB-9 spent sorbent from the CAFB gasification pilot plant.[3,9,12] Table 19 summarizes some of these dead-burned samples and compares their chemical compositions, especially sulfide and sulfate contents, with the original spent sorbent before dead-burning. Two points should be made: the dead-burning process reduced the sulfide content to negligible levels, and dead-burning at 1250°C increased the sulfate content in the stone and at 1550°C decreased the sulfate content. These are clear in the light of the CaS oxidation at 1250°C and $CaSO_4$ decomposition at 1550°C. Table 20 summarizes the leachate characteristics of these samples. The stones sintered at temperatures equal to or above 1250°C contained CaS sufficiently low that no measurable sulfide was found in their leachates. Leachates from stones sintered at 1550°C contained no detectable sulfide and also had a sulfate level below the DWS.

Although the leachate sulfide and sulfate were reduced by dead-burning processing, the pH, calcium, and TDS were not satisfactorily improved because of the formation of $Ca(OH)_2$.

Another observation worth noting is that the dead-burned samples before leaching were grey, lumpy solids whose darkness increased with the degree of sintering. The solids after leaching, however, were significantly swollen, ranging from an off-white fluffy mass to a pure white, crystalline powder in the reverse order - in other words, the whitest powder was the leached sample sintered at the highest temperature for the longest time. One possible explanation may be that the hydration and carbonation rates are decelerated by the degree of sintering; therefore, the whiter, more crystalline products were formed by the slower reaction during leaching of the more dead-burned spent sorbents.

The residual solids after leaching were determined by X-ray diffraction, TGA, and wet-chemical methods to consist of $Ca(OH)_2$ and $CaCO_3$ as major species. Figure 17 shows TG curves of some processed CAFB-9 spent stones. The top two curves show thermodecomposition of the residual solid after 200-hr aerobic leaching of dry-sulfation samples. A small amount of $CaCO_3$ is seen to decompose at point c for

Table 19

COMPARISON OF CHEMICAL COMPOSITIONS OF CAFB-9 SPENT SORBENT BEFORE AND AFTER DEAD-BURNING

Initial CAFB Particle Size, μm	Sintering Temperature, °C	Chemical Composition, wt %, before Leaching		
		Sintering Time, hr	$S^{=}$	$SO_4^{=}$
0 to 44	1250	2	0.0006	7.08
0 to 44	1250	5	0.0004	8.64
0 to 44	1250	24	0.009	8.52
0 to 44	1550	2	0	0.48
0 to 44	1550	5	0	0.6
0 to 44	1550	24	0	0.48
63 to 88	1250	2	0.0428	7.296
63 to 88	1250	5	0.0216	7.368
63 to 88	1250	24	0	6.552
63 to 88	1550	2	0.006	0.96
63 to 88	1550	5	0.0186	1.032
63 to 88	1550	24	0	0.984
CAFB-9 0-3000	Spent sorbent before dead-burning		2.24	3.07

Table 20

LEACHATE CHARACTERISTICS OF DEAD-BURNED CAFB-9 STONES

Dead-Burning Conditions	Leaching Conditions	Leachate Characteristics, mg/l)					
		pH	Sp. Cond. (μmhos/cm)	Ca	Mg	$S^{=}$	$SO_4^{=}$
0 to 44 μm, 1250°C, 2 hr	2 g/100 ml/430 hr/aerobic	12.5	8010	988	<5	<5	1042
0 to 44 μm, 1250°C, 5 hr	4 g/100 ml/430 hr/aerobic	12.5	7870	1362	<5	<5	1481
0 to 44 μm, 1250°C, 24 hr	4 g/100 ml/430 hr/aerobic	12.5	8290	1388	<5	<5	1486
0 to 44 μm, 1550°C, 2 hr	4 g/100 ml/430 hr/aerobic	12.6	8240	1274	<5	<5	1214
0 to 44 μm, 1550°C, 5 hr	2 g/100 ml/430 hr/aerobic	12.6	7590	360	<5	<5	134
0 to 44 μm, 1550°C, 24 hr	4 g/100 ml/430 hr, aerobic	12.6	7590	840	<5	<5	163
63 to 88 μm, 1250°C, 2 hr	4 g/100 ml/430 hr/aerobic	12.4	8520	1380	<5	<5	1560
63 to 88 μm, 1250°C, 5 hr	4 g/100 ml/430 hr/aerobic	12.4	8340	1322	<5	<5	1229
63 to 88 μm, 1250°C, 24 hr	4 g/100 ml/430 hr/aerobic	12.4	8340	1320	<5	<5	1428
63 to 88 μm, 1550°C, 2 hr	2 g/100 ml/430 hr/aerobic	12.5	7630	828	<5	<5	132
63 to 88 μm, 1550°C, 5 hr	2 g/100 ml/430 hr/aerobic	12.5	7940	844	<5	<5	113
63 to 88 μm, 1550°C, 24 hr	4 g/100 ml/430 hr/aerobic	12.6	7940	846	<5	<5	82

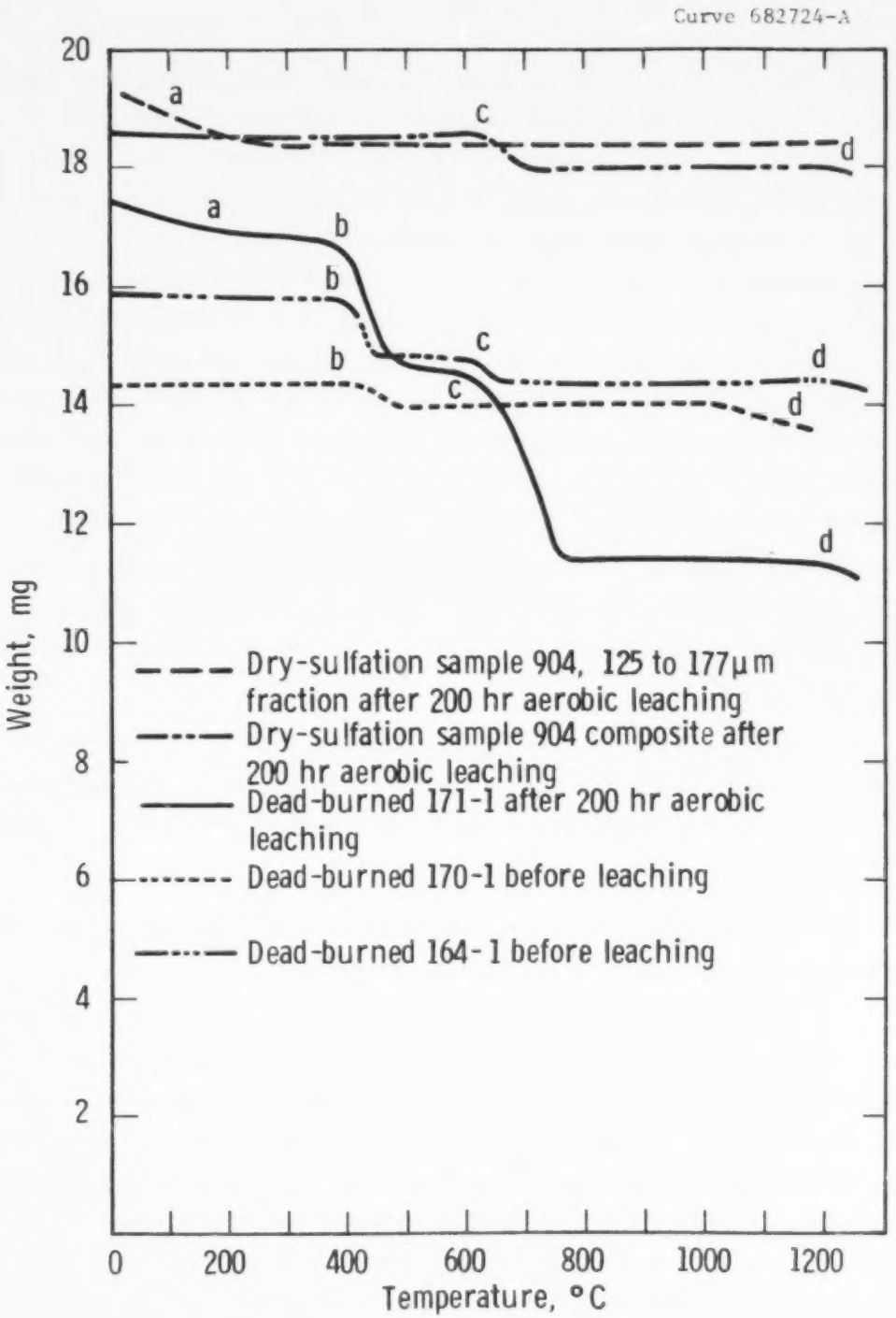

Curve 682724-A
Weight, mg
Temperature, °C
Dry-sulfation sample 904, 125 to 177µm fraction after 200 hr aerobic leaching
Dry-sulfation sample 904 composite after 200 hr aerobic leaching
Dead-burned 171-1 after 200 hr aerobic leaching
Dead-burned 170-1 before leaching
Dead-burned 164-1 before leaching

Figure 17 - Thermogravimetric Curve of Processed Spent Stones

sample 904 composite, and the major component, $CaSO_4$, begins to decompose at point d. Dead-burned sample 171-1 (1550°C, 24 hr) after 200 hours of aerobic leaching is shown to consist of a small amount of surface water at point a, major $Ca(OH)_2$ at b, $CaCO_3$ at c, and some $CaSO_4$ starting to decompose at point d. Dead-burned sample 170-1 (1550°C, 5 hr) before leaching is shown to contain some $Ca(OH)_2$, and dead-burned sample 164-1 (1070°C, 5 hr) before leaching contains both $Ca(OH)_2$ and $CaCO_3$, indicating that hydration and carbonation take place in air even with dead-burned spent stone. This finding illustrates the point that the dead-burning process up to 1550°C and 24 hours does not permanently deactivate the stone but merely slows down the hydration rate so that no immediate heat release is detected on contact with water.

No gaseous H_2S was detected (<1 ppm) during leaching. The aerobic leachate contains slightly less calcium, sulfate, and TDS than the anaerobic leachate. Trace metal ions in leachate would be no problem.

ERCA conducted "weathering" tests of the sintered spent stone by exposing the residue to outdoor conditions.[10] Table 21 compares the environmental impact projected by Westinghouse and ERCA.

Room-Temperature Ash Blending

Solid compacts can be formed by blending the spent CAFB stone with fly ash and casting them at room temperature.[3,9,12]

Nine solid compacts prepared from three proportions of spent sorbent and fly ash mixtures and cured in water for three lengths of time were investigated for their leaching behavior. Table 22 summarizes the results.[3,9,12] Two methods of leaching were adopted. In the first, the solid compact was ground to powder, and the standard shaking method was then applied. In the second, a chunk of the compact was broken off and then immersed in a flask of deionized water. The mixture that had the same solid-to-water ratio as the powder/water mixture was kept

Table 21

ENVIRONMENTAL IMPACT OF SINTERED (DEAD-BURNED) SPENT SORBENT

	(W) Laboratory-Scale Test	ERCA Weathering Test
Heat Release	• Nonsintered stone, $T_{3g/20\ ml} = 18°C$ • Sintered stone $T_{3g/20\ ml} < 0.2°C$	• Nonsintered T = 30°C (1st hr) • Sintered T = 5°C (20 hr)
$Ca(OH)_2/CaCO_3$ Formation	• Hydration of sintered CaO followed by carbonation takes place during leaching (because sintered stone is not truly dead-burned)	• All sintered CaO converts to $Ca(OH)_2$ in 2 mos; 50% $Ca(OH)_2$ converts to $CaCO_3$ in 12 mos. weathering
Sintering Temp.	• Sintering at 1250°C converts CaS to $CaSO_4$ • Sintering at 1550°C decomposes $CaSO_4$ to CaO	• Sulfide/sulfate content unclear
	• Leachate of 1250°C sintered stone contains high SO_4 • Leachate of 1550°C sintered stone contains little SO_4	• Sintering temp. 1350-1550°C had no effect on weathering (SO_4 in leachate not measured)
Trace Metal Elements	• Meet drinking water standards	• Not monitored extensively
Major Concern	• High pH, TDS, Ca in leachate	• High pH, Ca in leachate (TDS not determined)
Long-Term Weathering	• Environmentally stable $CaCO_3$ will eventually be formed	• $CaCO_3$ increases with weathering; $Ca(OH)_2$ decreases after peaking at 2 mos.

Table 22

Dwg. 1704834

LEACHATE CHARACTERISTICS OF ROOM-TEMPERATURE PROCESSED SOLID COMPACTS OF CAFB-9 REGENERATOR STONE AND FLY ASH

Duration / Sample	Leaching Conditions			Leachate Characteristics, mg/l					
	Solid Form	Shaking	Solid/Water	pH	Sp. Cond., μmhos/cm	Ca	Mg	$S^=$	SO_4
4A - 7 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.5	8090	1360	0	< 0.1	1613
4A - 7 days	Crushed powder	Yes	10 g/100 ml/256 hr aerobic	12.6	8440	1488	0	< 0.1	1987
4A - 14 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.4	8440	1380	0	0	1752
4A - 14 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.4	8540	1440	0	0	1920
4A - 28 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.3	8000	1296	0	0	1766
4A - 28 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.4	8400	1360	0	0	1814
4B - 7 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.5	8770	1600	0	< 0.1	2189
4B - 7 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.5	8810	1680	0	0.1	2438
4B - 14 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.4	8730	1456	0	0	1872
4B - 14 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.4	8700	1488	0	0	1968
4B - 28 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.3	8290	1336	0	0	1752
4B - 28 days	Powder	Yes	10 g/100 ml/256 hr	12.4	8740	1464	0	0	1944

Table 22 (Cont)

Dwg. 1704835

Duration / Sample	Leaching Conditions			Leachate Characteristics, mg/l					
	Solid Form	Shaking	Solid/Water	pH	Sp. Cond., µmhos/cm	Ca	Mg	$S^=$	SO_4
4C - 7 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.6	7970	1328	0	< 0.1	1680
4C - 7 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.5	8070	1440	0	< 0.1	1877
4C - 14 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.3	7770	1208	0	0	1584
4C - 14 days	Powder	Yes	10 g/100 ml/256 hr aerobic	12.4	8350	1404	0	0	1920
4C - 28 days	Chunk	No	10 g/100 ml/256 hr aerobic	12.4	8320	1328	0	0	1512
4C - 28 days	Powder	Yes	10 g/100 ml/256 hr	12.4	8250	1296	0	0	1632

without shaking for the same leaching time and its filtrate analyzed for leachate qualities. Examination of the results summarized in Table 22 reveals:

- Leaching for 256 hours using either one of the above methods produced leachates of similar quality, indicating that the solid compacts were permeable to water. The equilibrium state was reached for both mixtures.
- All nine samples (of three mixtures and three curing times) produced similar leachates, further indicating that a leachate saturation had been reached.
- Sulfide was low in all the solid blends studied and was undetectable in their leachates.
- All leachates were high in pH, calcium, sulfate, and TDS.
- Trace metal leachability is not expected to cause water contamination.

It appears that the leachates produced from these solid compacts are not as desirable as the leachates from either the sulfated sorbents, which had lower pH, calcium, and TDS, or the dead-burned stones, which had lower calcium and sulfate dissolution. It would be premature, however, to judge the potential usefulness of this utilization processing method based on the above results, which were obtained at the initial developmental stage.

High-Temperature Compacting

CAFB residue can also be processed by isostatic pressing at high temperature.[3,9,12] Solid compacts of high-temperature processed $CaSO_4$ and CAFB spent sorbents with fly ash were studied for their permeability and leaching behavior. Table 23 summarizes the sample preparation and resultant compositions as determined by X-ray diffraction. Obviously, the solid reaction took place during hot pressing; the major species present in 75-CF-26 and 75-CF-30 were $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$, which are the reaction products between the spent sorbent and fly ash.

Table 23.

PREPARATION AND COMPOSITIONS OF HIGH-TEMPERATURE PROCESSED SOLID COMPACTS

Samples	Sample Description	X-Ray Identification
75-CF-22	80% CaS + 20% coal fly ash, ball-milled for 2 hr, sieved to -120 mesh and hot pressed at 1050°C, 33096 kPa (4800 psi) for 1 hr d = 2.550 g/cm^3 Dark, hard, dense cylinder Smells of H_2S	Major CaS
75-CF-26	50% $CaSO_4$ + 50% coal fly ash, prepared under same conditions as above. d = 2.350 g/cm^3 Dark, hard dense cylinder No smell	Major $Ca_2Al_2SiO_7$ Minor $CaAl_2SiO_6$ SiO_2
75-CF-30	20% CAFB-9 spent sorbent + 80% coal ash, prepared under similar conditions as above. d = 2.460 g/cm^3 Dark, hard, dense cylinder No smell	Major $Ca_2Al_2SiO_7$ $CaAl_2Si_2O_8Fe$ Minor $CaAl_2SiO_6SiO_2$

Preliminary testing indicated a very low permeability coefficient, in the order of 10^{-8} cm/s. Leachate characteristics are presented in Table 24. A significant difference was found between the leachates induced by the two procedures: static contact of water with cylindrical samples versus shaking of crushed powder in water, with the former resembling the more realistic landfill situation and the latter representing the worst possible case. This result further indicates low sample permeability. Of these three samples, the leachability of 75-CF-30 is of primary interest because it is made of CAFB spent sorbent. The leachate of this sample is low in TDS, calcium, sulfate, and sulfide, passing the DWS even when induced by the shake (crushed sample) method.

Table 24

LEACHATE CHARACTERISTICS OF HIGH-TEMPERATURE SOLID COMPACTS OF SORBENT/ASH MIXTURE

Sample	Sample Conditions	Leaching Procedure*	Solid/H_2O Ratio	Leaching Time, hr	Leachate Characteristics					
					pH	Sp. Cond., $\mu mhos\text{-}cm^{-1}$	Ca, mg/ℓ	Mg, mg/ℓ	$S^{=}$, mg/ℓ	$SO_4^{=}$, mg/ℓ
75-CF-22	Crushed powder	A	1:10	210	11.35	14700	4964	19	1925	6528
"	Cylindrical sample	B	1:10	210	9.96	410	64	<10	30	152
75-CF-26	Crushed powder	A	1:10	210	8.02	950	108	0	61	389
"	Cylindrical sample	B	1:10	210	9.68	290	<10	<10	<20	90
75-CF-30	Crushed powder	A	1:10	210	8.35	520	72	24	34	233
"	Cylindrical sample	B	1:10	210	9.28	90	<10	<10	< 5	22

*Procedure A: Solid-water mixtures are agitated in Erlenmeyer flasks by an automatic shaker; mixtures are filtered for leachate analysis.

*Procedure B: The cylindrical sample is mounted at the bottom of a glass tube with only the top surface in contact with water. No agitation is applied. As the samples are practically impermeable, leachates are poured out for analysis.

In summary, the high-temperature processed solid compacts of spent sorbent and fly ash are more stable on contact with water than are the spent sorbent and fly ash separately, due to the formation of the insoluble cementlike calcium-aluminate-silicate compounds. Leaching results indicated satisfactory leachates with reduced pH, TDS, calcium, sulfide, and sulfate concentration. Trace elements also pass DWS. The potential application of this processing method, however, would also depend on the results of economic analysis.

Slurry Carbonation

Slurry carbonation is a processing method whereby the spent sorbent is carbonated with CO_2 to form practicably insoluble $CaCO_3$.[3] On the basis of the results obtained, few environmental problems are expected:

- Of the total spent sorbent, 96 to 97 percent can be converted to practically insoluble and environmentally stable $CaCO_3$, whose leachate is expected not to cause water contamination.
- CaS in the spent sorbent is converted to H_2S during the slurry carbonation reaction; it is recycled to the gasifier and sent to the S-recovery system. No or low sulfide in the leachate is expected.
- Since the heat of hydration of CaO is released during the slurry carbonation reaction (which is utilized as a heat source), disposal of the carbonated sorbent will not cause heat pollution.
- Leachability of trace metal elements is expected to be similar to that of the unprocessed spent sorbent, which has been shown not to be of environmental concern.

Reference Material

TUGCO Ash

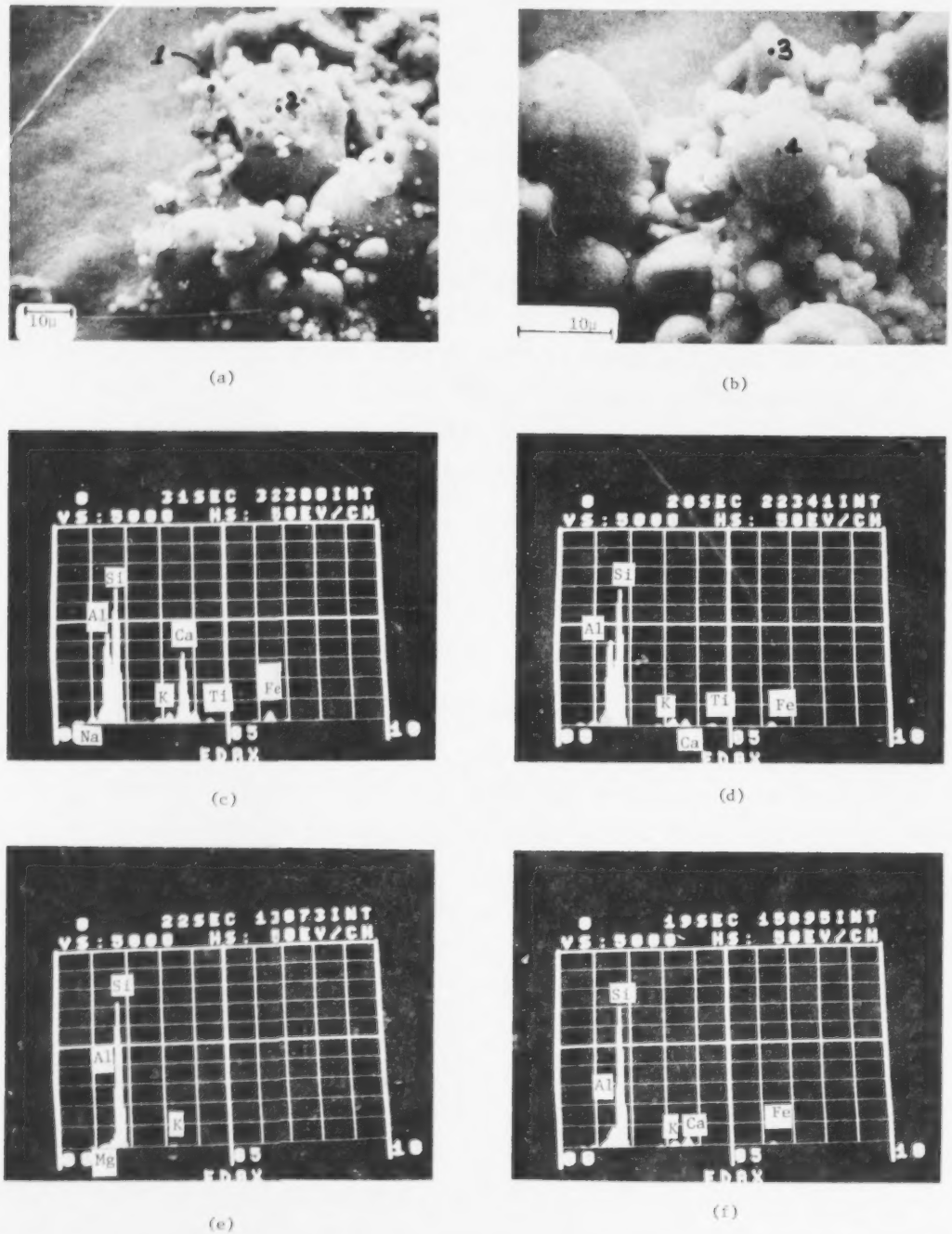
Characterization of the coal ash from TUGCO,[31] and tests on the environmental impact of land disposal were carried out. The objective was to provide references to the leaching and activity properties of the fly ash resulting from the CAFB process utilizing Texas lignite coal as the solid fuel.

X-ray diffraction showed that the ash consisted of major SiO_2 (quartz) and minor $Al_2O_3 \cdot 2\ SiO_2$ (mullite). Results by wet chemistry analysis are shown in Table 25. Morphological investigation reveals that the TUGCO ash is composed of cenospheres ranging from 0.1 to 40 μm in size. Figure 18 shows typical SEM photomicrographs of the sample and EDAX spectra of four cenospheres of different diameters. Note that silicon and aluminum are the major elements present in all four sites scanned and that the minor elements (calcium, potassium, iron, magnesium, and titanium) vary among particles.

Table 25

ANALYSIS OF TUGCO ASH

Substance	Wt %
S_iO_2	60.4
Al_2O_3	19.3
Fe_2O_3	2.54
CaO	9.36
MgO	2.27
SO_3	0.05
P	0.029
F	0.016
Cl	<0.001
Others	6.03



(a) (b)

(c) (d)

(e) (f)

Figure 18 - Typical SEM and EDAX of TUGCO Ash; (a) and (b), SEM; (c), (d), (e), and (f), EDAX Spectra Scanned on Sites 1, 2, 3, and 4, Respectively

Leaching studies were carried out employing both the continuous and intermittent shake procedures. Table 26 summarizes the results of the continuous shake test. Figure 19 shows the results of the intermittent leaching test. Both tests resulted in relatively pure leachates with lower pH, calcium, SO_4, and TDS than the typical leachate of spent sorbent or ash from the CAFB process. The higher pH, calcium, SO_4, and TDS from the spent CAFB solid are caused by the CaO, CaS, and $CaSO_4$ present in the utilized sulfur removal sorbent. The trace metal elements present in the TUGCO ash and its leachate are summarized in Table 27. Two elements, chromium and selenium, are found to exceed the drinking water standards.

No detectable heat-release activity was found when TUGCO ash came into contact with water.

Valley Builder Supply Samples

Characterization of the samples obtained from Valley Builder Supply[31] has been completed and the environmental impact has been investigated to provide a reference for the disposal of processed and utilized CAFB residue. Table 28 lists the samples obtained and summarizes the chemical compositions as determined by X-ray diffraction and wet chemical methods. Figures 20a and b show typical optical and SEM microphotographs of a piece broken from the Valley Builder block. Figures 20c and d show, respectively, the porous area A and the less porous area B identified on 20b. EDAX analysis shows the porous area A is rich in silicon and aluminum, plus potassium, iron, and calcium in decreasing order; and the less porous area B is rich in calcium, with silicon, aluminum, potassium, and iron in decreasing concentrations.

Standard leaching tests were carried out on a piece of Valley Builder block, both as it is and as crushed powder. Table 29 summarizes the chemical characteristics of the block and its leachates and compares the leachates with the DWS. The leachates exceed DWS for pH although

Table 26

CHEMICAL CHARACTERISTICS OF LEACHATE FROM TUGCO ASH
BY CONTINUOUS SHAKE TEST

Leach Conditions	Leachate Characteristics, mg/ℓ												
	pH	Spec. Cond. (μmhos/cm)	Ca	Mg	$S^{=}$	SO_4	F	Cl	Br	NO_2	NO_3	PO_4	TOC
50 g/500 ml, 200 hr	10.7	810	144	<10	<10	263	<1	<1	<1	<1	<1	<1	<10
10 g/100 ml, 400 hr	8.2	760	148	10	10	← Not Determined →							

Curve 692873-B

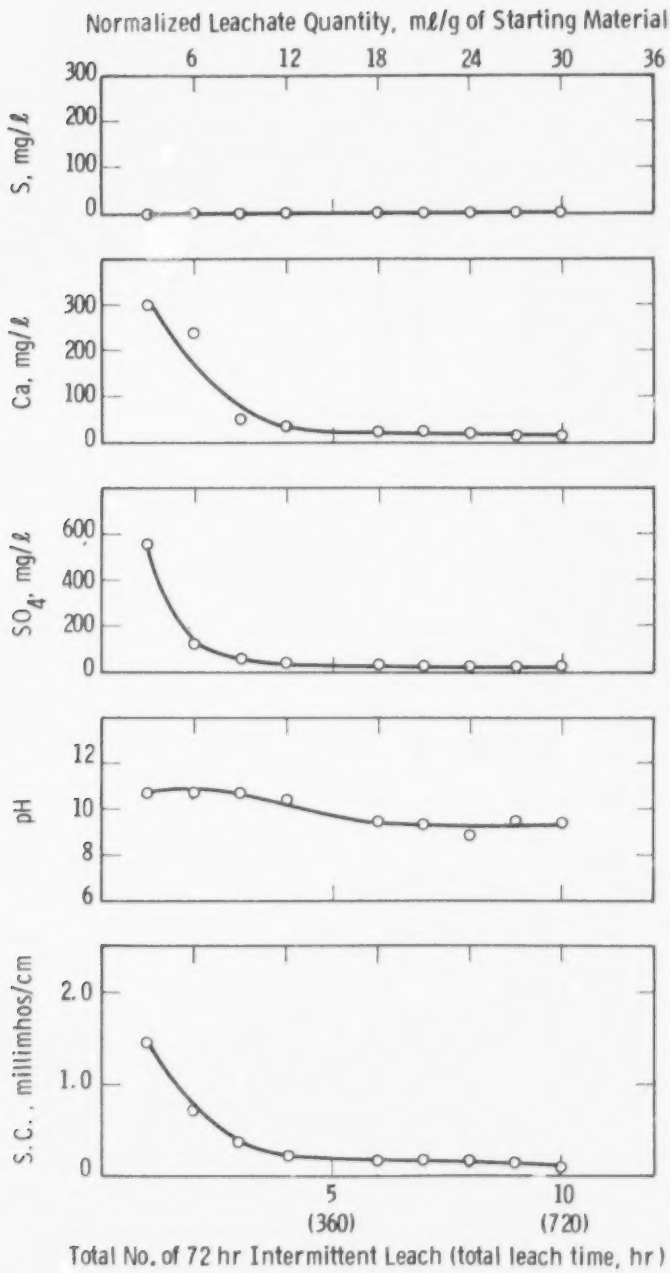


Figure 19 - Leachate Characteristics of TUGCO Ash

Table 27

TRACE METAL ELEMENTS IN TUGCO ASH AND ITS LEACHATE

Substance	TUGCO Ash Solid, ppm	TUGCO Leachate, ppm
Al	Major	> 1
Ag	< 1	< 0.01
As	12.1	0.006
B	500	> 1
Be	5	< 0.01
Bi	< 10	< 0.01
Ca	Major	Major
Cd	< 3	< 0.01
Co	20	< 0.01
Cr	80	0.7[a]
Cu	200	< 1
Fe	Major	< 0.1
Hg	0.12	< 0.001
Mg	≥ 1000	< 1
Mn	660	< 0.01
Mo	30	0.2
Na	> 1000	≈ 1
Ni	50	< 0.05
Pb	85	< 0.01
Sb	< 33	< 0.05
Se	4.0	0.05[a]
Si	Major	< 1
Sn	< 10	< 0.05
Sr	1000	> 1
Ti	< 1000	< 1
V	250	0.5
Zn	100	< 1
Zr		< 1

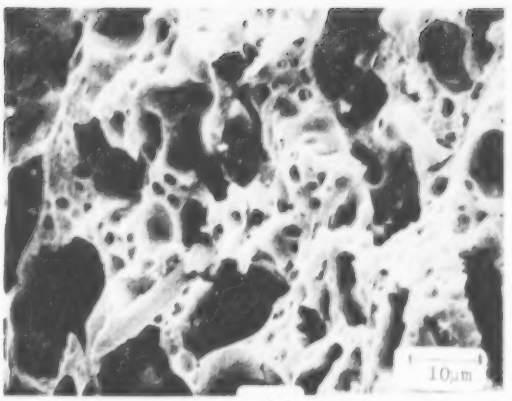
[a]Exceed the U.S. Drinking Water Standards for Cr (0.05 ppm) and Se (0.01 ppm).

Table 28

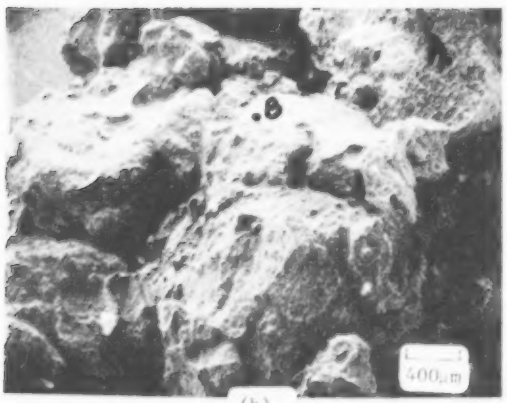
CHEMICAL COMPOSITIONS OF VALLEY BUILDER SUPPLY SAMPLES

Samples	X-Ray Diffraction	Wet Chemistry, wt %				
		Ca	Mg	$SO_4^=$	$S^=$	$CO_3^=$
Limestone Dust		37.28	1.0	0.02	0.03	58.39
Type I Cement	(Major) 54 CaO · 16 SiO_2 · MgO · Al_2O_3 and/or Ca_3SiO_3 and others in trace amounts (SiO_2, $CaCO_3$, $Ca(OH)_2$, $CaSO_4$, $CaSO_4 \cdot 2H_2O$, $Ca_3Mg(SiO_4)_2$, CaO, and $(Mg, Fe)_2SiO_4$)	43.68	2.4	3.4	0.04	0.82
Fine Aggregate	Major SiO_2 quartz and an unidentified trace phase	0.96	0.19	0.22	0.1	0.71
Coarse Aggregate		0.8	0.19	0.83	0.08	0.52
Block	Major SiO_2 quartz, trace $CaCO_3$ calcite	8.0	0.19	0.21	0.05	7.55

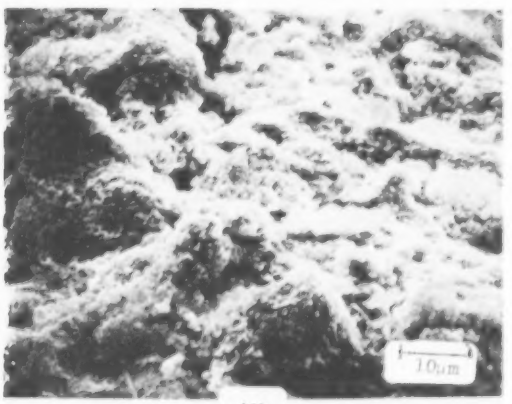
(a)



(c)



(b)



(d)

Figure 20 - Valley Builder Supply Block: (a) Optical photomicrograph at 3X; (b) SEM at 26X; (c) porous area A at 1300X, rich in Si, Al, plus K, Fe and Ca in decreasing concentrations shown by EDAX; (d) less porous area B at 1300X, rich in Ca, also Si, Al, K, Fe in decreasing concentrations.

Table 29

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CHEMICAL CHARACTERISTICS OF VALLEY BUILDER SUPPLY BLOCK AND LEACHATE

Substance	Solid, ppm	Leachate, ppm		*Drinking Water Standards, ppm
		a	b	
Ag	<1	< 0.01	< 0.01	0.05
Al	Major	<1	<1	
As		< 0.01	< 0.01	0.05
B	350	<1	<1	
Ba	500	<1	<1	1.0
Be	2	< 0.01	< 0.01	
Bi	1	< 0.01	< 0.01	
Ca	8.0%	52	114	200
Cd	<1	< 0.01	< 0.01	0.01
Cr	20	0.02	0.04	0.05
Cu	30	<1	<1	1.0
Fe	>1%	< 0.2	< 0.2	0.3
Hg		< 0.002	< 0.002	0.002
Mg	0.19%	<10	<10	150
Mn	100	< 0.01	< 0.01	0.05
Mo	20	< 0.05	< 0.05	
Ni	20	< 0.05	< 0.05	2.0
Pb	10	< 0.01	< 0.01	0.05
Sb	<10	< 0.2	< 0.2	
Se		< 0.01	< 0.01	0.01
Si	Major	< 0.01	< 0.01	0.01
Sn	<3	< 0.2	< 0.2	1.0
Sr	>300	<1	<1	
Ti	>1000	< 0.2	< 0.2	
V	150	0.05	0.2	
Zn	100	<1	<1	5.0
Zn	500	<1	<1	5.0
Cl		2.6	4.2	250
F		<1	<1	2.4
S =	0.05%	<10	<10	
SO_4	0.21%	35	194	250
TOC		<5	<5	
pH		10.41	9.62	5.0 to 9.0
Sp. Cond. µmhos/cm		270	420	~750

*DWS-----NIPDWR, USPHS, and WHO Drinking Water Standards

a -----leachate from a piece of uncrushed block

b -----leachate from crushed powder

▨ -----exceeds the DWS

much less than does the CAFB leachate. One may recall that a typical CAFB leachate (processed and unprocessed) exceeds the DWS for pH, calcium, SO_4, and TDS.

Results from the heat-release tests are summarized in Table 30. The limestone dust and fine and coarse aggregates did not show any temperature rise; the cement powder gave off heat on contact with water as expected. The block (after being crushed to powder), however, also showed a very slow temperature rise when exposed to water.

Table 30

HEAT-RELEASE PROPERTIES OF VALLEY BUILDER SUPPLY SAMPLES

Samples	Heat-Release, ΔT, °C	
	3 g/20 ml	16 g/4 ml
Limestone Dust	<0.2°C	<0.2°C
Type I Cement	2°C (immediate rise)	6°C in < 1.5 min
Fine Aggregate	<0.2°C	<0.2°C
Coarse Aggregate	<0.2°C	<0.2°C
Block	<0.2°C	<0.2°C
Block (crushed powder)	<0.2°C	2°C slow rise over 1.5 hr

FGD Sludge

In the absence of leachate criteria with which to assess the environmental acceptability of land disposal of CAFB residue, the leaching property of residues from conventional coal-burning power plants with flue gas desulfurization scrubber systems has been investigated to provide a reference for the leachate characteristics of residue from a currently commercialized process.

A typical untreated FGD sludge using lime or limestone sorbent contains 30 to 70 percent solid matter after settling. The major constituents of the solid are $CaSO_3 \cdot 1/2\ H_2O$, $CaSO_4 \cdot 2\ H_2O$, $CaCO_3$; coal ash that consists of SiO_2, Al_2O_3, Fe_2O_3; and trace elements. The exact composition varies, depending on many factors, including the type of coal, the type of scrubber system, and boiler and scrubber operating conditions.

Six samples of FGD sludge from pilot- and commercial-scale SO_2 scrubbing systems, including untreated, ponded, oxidized, and stabilized lime or limestone scrubber sludges, were tested during the investigation. Table 31 summarizes the sample source, scrubber system, further treatment, and X-ray identification of the sludges. All sludge samples except one (the stabilized) were wet with supernatant liquors as received. The liquors were separated by vacuum filtration and analyzed chemically. The dewatered sludges were then dried (~95 to 105°C), and the sludge powders underwent the standard leaching tests developed for CAFB residues.

SEM of the unprocessed sludge (Figure 21) shows the small platelet crystallites of $CaSO_3 \cdot 1/2\ H_2O$ that have been reported by the FGD investigators[39-41] to be responsible for the dewatering/settling difficulties and the thixotropic property of the sludge. The ponded sludge often has mixtures of the flaky platelets and bulkier crystals due to partial oxidation of sulfite to sulfate. On the other hand, the oxidized TVA sludge shows large crystals of gypsum ($CaSO_4 \cdot 2\ H_2O$). The potential environmental hazard (due to sulfite oxygen demand) has been reduced, and dewatering and settling difficulties are greatly improved. In fact, oxidation to gypsum has been recommended as one of the methods by which to stabilize FGD sludge.[46] Cenospheres from coal ash are also present in the sludge samples and may also cause settling problems in ponding. EDAX spectra show that the platelet crystallites of the FGD solid are high in calcium and sulfur (presumably $CaSO_3 \cdot 1/2\ H_2O$) and that the cenospheres are rich in silicon, aluminum, and iron (coal ash).

Table 31

SUMMARY OF FGD SLUDGE SAMPLES

Sample	Process Description	X-Ray Identification
Louisville Gas and Electric Company (LGE)[42]	Fresh, untreated, unponded; lime sludge with small amount of MgO added	Major: $CaSO_3 \cdot 1/2\ H_2O$ Low minor: $(Fe,Mg)\ Al_2O_4$ or $(Mg,Fe)\ SiO_4$ spinel
Columbus Southern Ohio Company (CSO)[43]	Untreated lime sludge; 98% fly ash removal	Major: $CaSO_3 \cdot 1/2\ H_2O$
Duquesne Light Company (DLC)[43]	Untreated lime sludge; containing ~50% fly ash	Major: SiO_2 Minor: $CaSO_3 \cdot 1/2\ H_2O$ Low minor: Fe_2O_3
TVA Shawnee, Pond E[44,45]	Untreated, ponded limestone sludge bottled in pond liquor for 2.5 yr	Major: $CaSO_3 \cdot 1/2\ H_2O$ Major: $CaCO_3$ Trace: SiO_2
TVA Shawnee - Oxidized Sludge[44,45]	Lime sludge followed by forced air oxidation to gypsum	Major: $CaSO_4 \cdot 2\ H_2O$
Duquesne Light Company[43] - Stabilized Sludge	"Calcilox" stabilized lime sludge containing ~50% fly ash; stabilized and ponded for 3 yr	Major: SiO_2, amorphous phase Minor: $CaCO_3$, $CaSO_3 \cdot 1/2\ H_2O$

SEM Photomicrographs of Dewatered FGD Sludge

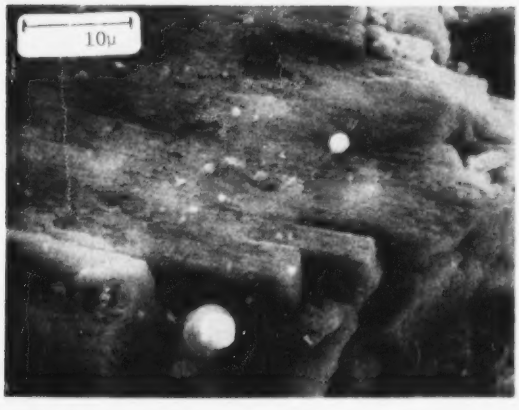
(a)

FGD sludge (LGE)
unponded, untreated

(b)

FGD sludge (TVA)
ponded, untreated

(c)



FGD sludge (TVA)
oxidized, gypsum

Figure 21 - SEM Photomicrographs of Dewatered FGD Sludge

SEM of the stabilized sludge shows a mixture of cenospheres and a fluffy mass that appears frequently to be clustered and to have adhered to the cenospheres. The platelet crystallites are no longer observed. It has been reported that the compressive strength of the stabilized sludge increases as a function of stabilization (solid setting) time.[47]

Leaching properties were investigated using both the continuous and the intermittent shake methods described in the previous section. Figure 22 shows the leachate characteristics of the dried sludge as a function of continuing leaching time. Note that the leachate from the stabilized FGD sludge is very similar to gypsum leachate. On the average the untreated sludge leachate has higher calcium, magnesium, SO_4, pH, and TDS.

Figure 23 shows the specific onductance and approximate TDS in the leachate from the intermittent shake test. The better leachate quality is seen again in the case of the stabilized sludge. The leachate from the untreated, ponded, and oxidized sludge had much higher TDS and improved with total leaching time and total leachate volume. The lower TDS in the CSO leachate after two 72-hr leach cycles was due to the low solubility of calcium sulfite ($CaSO_3$), which was the predominant specimen in the untreated fly-ash-free CSO sludge. It must be kept in mind that the leachate characteristics presented here were from the vacuum-filtered and dried sludge. The superheated liquors of the sludges had much higher TDS and specific ion concentrations, as seen in Table 32, which summarizes the chemical characteristics of the solid, liquor, and leachate of the untreated, ponded, oxidized, and stabilized sludge samples. One can see that the trace element concentrations are the lowest for the leachate from the stabilized sludge and next lowest in the untreated sludge following ponding. Although oxidation to gypsum increased the crystal size and improved the sludge settling property and shear stress,[46] the trace element and anion concentrations in the oxidized sludge liquor and leachate remained high.

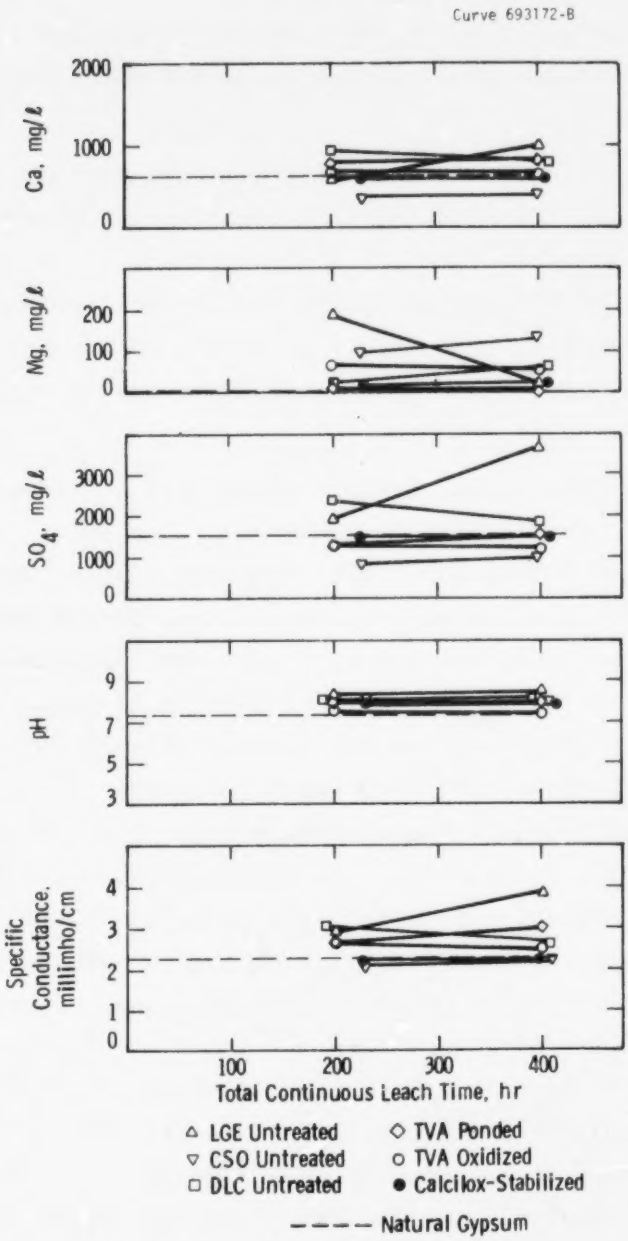


Figure 22 - Leachate Characteristics of Dried FGD Sludge as a Function of Continuous Leach Time

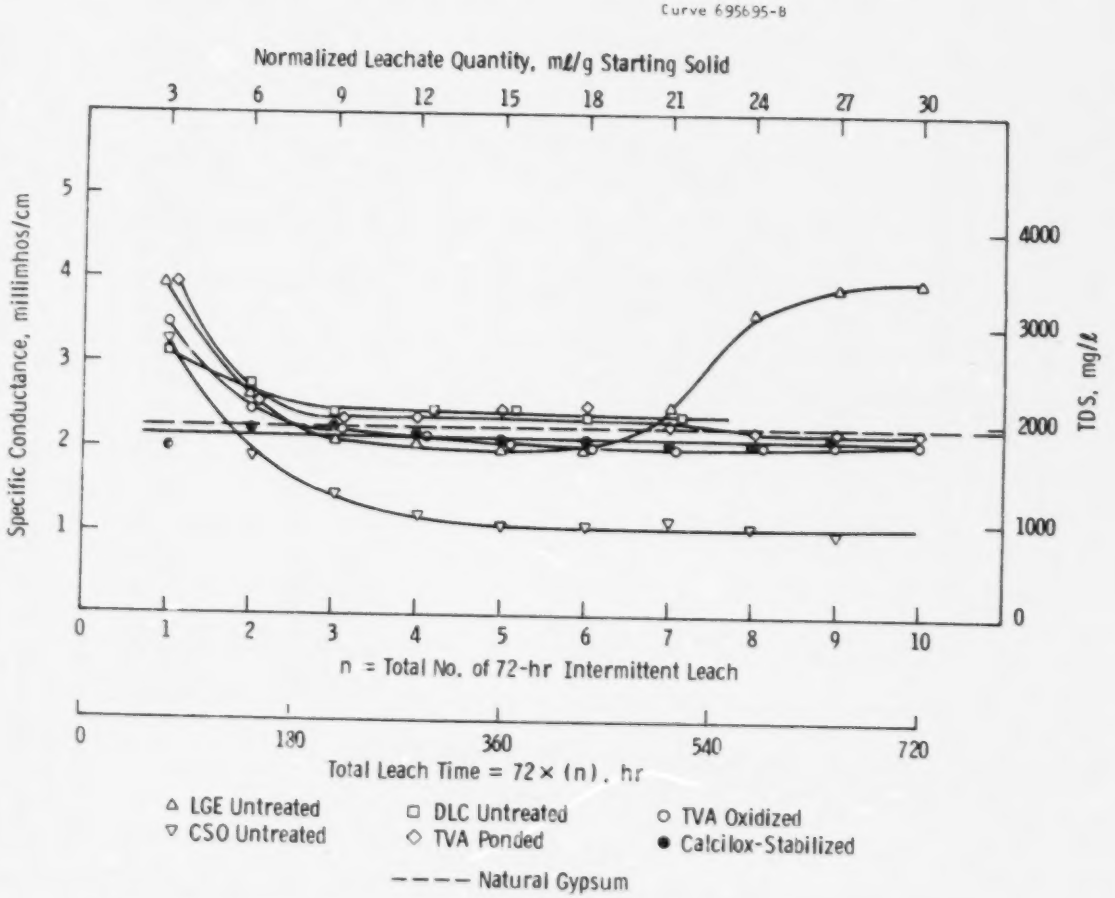

Curve 695695-B
Normalized Leachate Quantity, mℓ/g Starting Solid
3 6 9 12 15 18 21 24 27 30
Specific Conductance, millimhos/cm
5 4 3 2 1
4000 3000 2000 1000 0
TDS, mg/ℓ
0 1 2 3 4 5 6 7 8 9 10
n = Total No. of 72-hr Intermittent Leach
0 180 360 540 720
Total Leach Time = 72 × (n), hr
△ LGE Untreated
▽ CSO Untreated
□ DLC Untreated
◇ TVA Ponded
○ TVA Oxidized
● Calcilox-Stabilized
– – – – Natural Gypsum

Figure 23 - Leachate Characteristics of Dried FGD Sludge as a Function of Intermittent Leaching

Table 32

CHEMICAL CHARACTERISTICS OF FGD SLUDGE, LIQUOR, AND LEACHATE[a]

Substances	Sludge, ppm [a] (on dry basis)	Liquor, ppm			Leachate, ppm (of dried solid)			
		Untreated	Ponded	Oxidized	Untreated	Ponded	Oxidized	Stabilized [b]
Al	0.2 - 20%	< 2	0.4	20	< 1	< 1	< 1	< 1
Ag	< 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
As	3 to 30	0.03	0.03	0.01	0.01 to 0.06	0.09	0.01	0.05
B	30 to 300	1 to 20	> 7	> 20	0 to 2	> 3	> 1	1
Ba	10 to 1000	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Be	0 to 15	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1
Bi	< 10	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01
Ca	10 to 30%	500 to 1500	1824	2408	300 to 1000	760	660	630
Cd	< 3	< 0.01	< 0.02	0.2	< 0.01	< 0.01	< 0.01	< 0.01
Co	0 to 10	< 0.05	< 0.05	< 0.06	< 0.05	< 0.05	< 0.05	< 0.05
Cr	1 to 100	< 0.04	< 0.03	< 0.06	< 0.03	< 0.03	< 0.03	< 0.03
Cu	1 to 60	< 1	< 1	< 1	1	< 1	< 1	< 1
Fe	0.1 to 10%	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Hg	0.1 to 3	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Mg	0.1 to 10%	0 to 600	< 30	1104	10 to 250	< 30	200	16
Mn	10 to > 1000	0 to .07	0.02	20	< 0.05	< 0.05	< 0.07	< 0.05
Mo	0 to 20	< 0.5	7	0.7	< 0.2	< 0.2	0.1	0.3
Na	0.01 to 5%	0 to 100	111	106	5 to 15	5	3	6
Ni	0 to 30	< 1	< 1	< 1	< 0.05	< 0.05	< 0.05	< 0.05
Pb	0 to 200	< 0.95	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Sb	< 33	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Se	1 to 5	0.005 to 0.03	0.01	0.32	0.01 to 0.03	0.007	0.1	0.006
Si	0.5 to 20%	2 to 20	2.7	5	0.1 to 4	2	1	3
Sn	< 10	< 1.0	< 1.0	< 1.0	< .05	< 0.05	< 0.05	< 0.05
Sr	100 to 1000	< 2	> 7	40	< 1	1	2	
Ti	100 to > 1000	< 1	< 1	< 2	< 1	< 1	< 1	< 1
V	0 to 100	< 0.05	2	< 0.06	< 0.05	< 0.05	< 0.05	< 0.05
Zn	20 to 200	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Zr	1 to 1000	< 2	< 2	< 2	< 1	< 1	< 1	< 1
CO_3	0.1 to 15%							
SO_3	0.05 to 50%	0 to 40	< 10	< 10	< 10	< 10	< 10	< 10
SO_4	3 to 65%	1000 to 7000	1200	1450	500 to 2500	1100	1500	1400
Cl	0 to 1%	300 to 1000	2800	5100	30 to 120	180	170	2
Br		0 to 40			0 to 3			< 1
F	10 to 50	2 to 23	22	33	1 to 6	1.3	4.5	5
NO_3 (as N)		0 to 100	< 10	60	< 10	< 10	< 10	< 10
NO_2		0 to 40			< 10			< 10
PO_4		0 to 10			< 1			< 1
TOC		< 30	< 30	< 30	< 30	< 30	< 30	< 30
pH		8 to 10	8.6	6.1	7.5 to 8.5	8.0	8.2	8.0
Sp. Cond. (umhos/cm)		4000 to 9000	5920	16900	2000 to 3000	2640	2830	2350

a Based on analysis of 6 samples tested

b Chemically treated by Dravo's "Calcilox"

▨ Exceed Drinking Water Standards (NIPDWR, USPHS, and WHO)

The investigation of FGD residues presented in this section has been limited to their chemical and leaching properties. The physical properties of the FGD sludge have been reported in the literature.[45-47]

Gypsum

Granular gypsum (Iowa No. 114) was tested in parallel with many of the CAFB leaching tests to provide a reference for natural $CaSO_4$ leachability. Results have been reported in the previous sections.

Heat Release Property

The activity of residual lime in spent sorbents and fly ash was determined by its heat release property on contact with water, as the hydration reaction of CaO is extremely exothermic.[36] Literature on lime reactivity and slaking rate has been reviewed. The ASTMC110-76[37] provides a test for the slaking rate of quicklime (CaO). In this test 76 g of quicklime is added to 380 ml of distilled water in a modified Dewar flask covered with a rubber gasket fitted with a mechanical stirrer. The temperature is read with a thermometer at 30-second to 5-minute intervals, depending on the reactivity of the quicklime, until a constant temperature is reached. The slaking rate is determined by the following quantities: temperature rise at 30 seconds, total temperature rise, and active slaking time.

Murray[38] studied lime reactivity as a function of porosity and shrinkage characteristics during calcination and found that calcitic quicklime of low shrinkage and high porosity had high reactivity. He used a lime:water ratio of 1:7 by weight. Since preliminary slaking tests indicated a wide range in slaking rates, an empirical compromise point was selected as indicative of the rapidity of slaking. The temperature rise in five seconds was selected, and the reactivity coefficient was designated as ΔT_5; yet he readily acknowledges that

his test was inequitable for the extremely reactive limes in which slaking was actually completed in three to four seconds, so that a reading at five seconds made them appear to be slower than they actually were.

American Water Works' standard on lime for water treatment employs a lime slaking test with lime:water proportions 100 g:400 ml, following the test procedure of ASTMC110.

The temperature rise of a solid/water system containing free CaO is a function of solid:water ratio. In our experimental effort to establish a screening test for the residual activity in spent CAFB solids produced under varying processing conditions, a solid to water proportion of 3 g to 20 ml (which is in the bulk range specified by the ASTMC110 test and by Murray's work) was found empirically to provide much better repeatability than that from a higher solid:water ratio which would give greater temperature rise but would lack reproducibility, most likely because of local heating. The former ratio was initially adopted as the screening test for heat-release property because of its speed, small quantity of stone required, and the good reproducibility of results. The latter, however (small quantity of water added to larger quantity of solid), was also used because it provides higher sensitivity and simulates rainfall onto the disposed solid.

Figure 24 compares the temperature rise as a function of solid:water ratio for CAFB spent sorbent and a calcined limestone. Higher temperature rise and faster response are observed for the higher solid:water ratio system, as expected. Figure 25 shows the temperature rise profile when 4 ml of water are added to 16 g of six CAFB spent materials. A lower solid:water ratio is used for the calcined limestone for comparison due to the calcined limestone's extremely violent heat release characteristics. A variation in residue activity among different batches of CAFB spent sorbent was noted. Spent bed material also displays greater heat release property than did fly ash or stack fines.

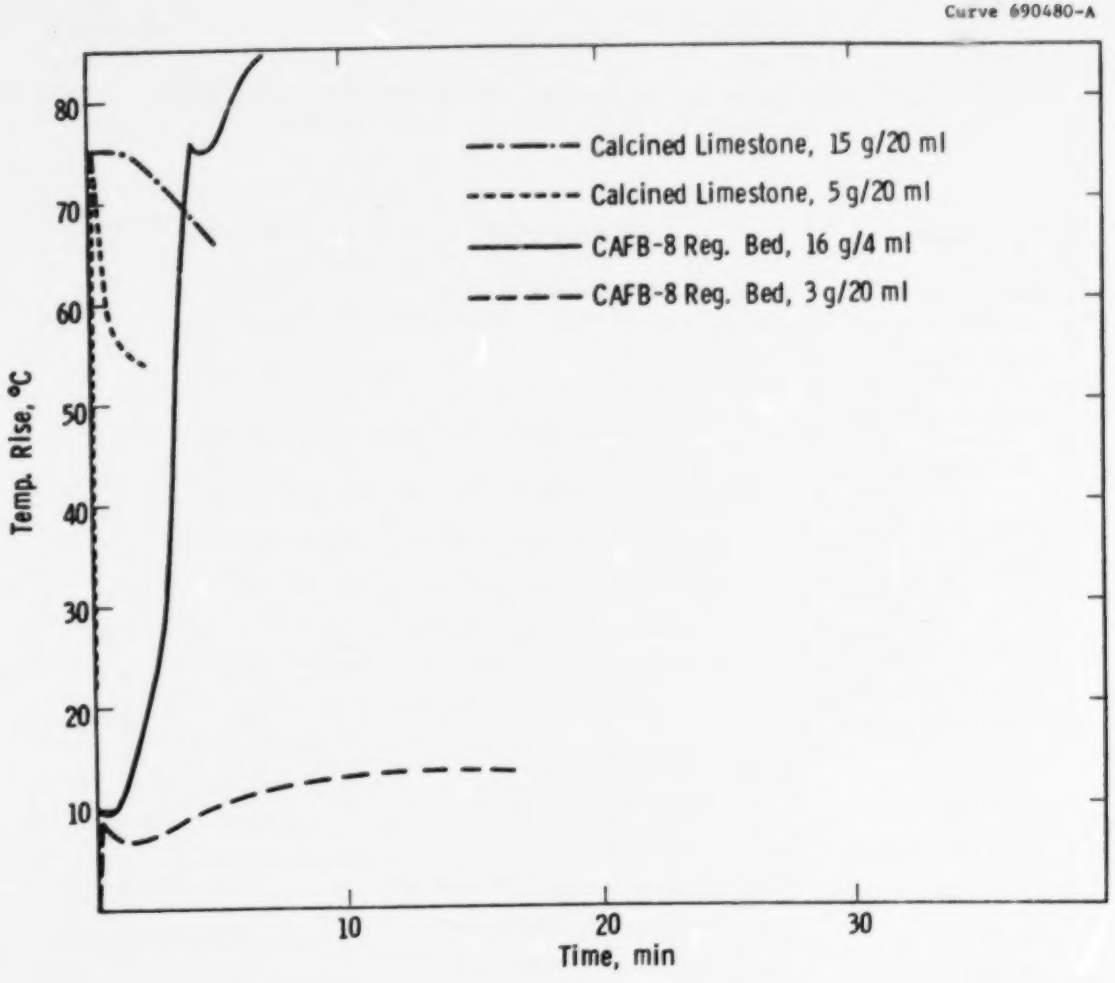


Figure 24 - Heat-Release Property as a Function of Solid:Water Ratio

The heat release properties of all the CAFB residues, processed and unprocessed, using the lower solid:water ratio (3 g:20 ml) are summarized in Table 33. Note the improvement by processing.

Total Dissolved Solids

The total dissolved solid (TDS) in a leachate is a good index of leachate quality. TDS, which can be determined by the time-consuming evaporating procedure, can be estimated by multiplying the easily measured specific conductance by an empirical factor. This factor may

Table 33

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ACTIVITY TESTS OF PROCESSED AND UNPROCESSED CAFB SPENT SORBENTS BY THEIR HEAT-RELEASE PROPERTIES

Samples	Processing History	Solid/Water	ΔT_{max}, °C
CAFB - 7 Reg. Bed	Unprocessed CAFB residue from ERCA	3 g/20 ml	18
CAFB - 8 Reg. Bed	"	"	10.3
CAFB - 8 Gasif. Bed	"	"	6.7
CAFB - 8 Stack Fines	"	"	3.1
CAFB - 9 Reg. Bed	"	"	15
CAFB - 10A Gasif. Bed	"	"	2
CAFB - 11 Reg. Bed	"	"	18
CAFB - 11 Gasif. Bed	"	"	20
CAFB - 11 Main Cyclone	"	"	1.3
CAFB - 11 Stack Fines	"	"	< 0.2
DS - Mix	76 m% sulfated CAFB - 7	"	< 0.2
CAFB - 903	50 m% sulfated CAFB - 9	"	0.7
CAFB - 904 Composite	79 m% sulfated CAFB - 9	"	< 0.2
CAFB - 904 125 - 177 µm	CAFB - 904 sieved to + 125 − 177µm, 94 m%	"	< 0.2
DB 163	Dead-burned CAFB - 9, 1070°C, 2 hr	"	17
DB 164	Dead-burned CAFB - 9, 1070°C, 5 hr	"	19
DB 165	Dead-burned CAFB - 9, 1070°C, 24 hr	"	0.9
DB 166	Dead-burned CAFB - 9, 1250°C, 2 hr	"	7.2
DB 167	Dead-burned CAFB - 9, 1250°C, 5 hr	"	< 0.2
DB 168	Dead-burned CAFB - 9, 1250°C, 24 hr	"	< 0.2
DB 169	Dead-burned CAFB - 9, 1550°C, 2 hr	"	< 0.2
DB 170	Dead-burned CAFB - 9, 1550°C, 5 hr	"	< 0.2
DB 171	Dead-burned CAFB - 9, 1550°C, 24 hr	"	< 0.2

Table 33 (Continued)

Dwg. 1704B55

Samples	Processing History	Solid/Water	ΔT_{max}, °C
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1250°C, 2 hr	3 g/20ml	< 0.2
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1250°C, 5 hr	"	< 0.2
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1250°C, 24 hr	"	< 0.2
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1250°C, 2 hr	"	< 0.2
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1550°C, 5 hr	"	< 0.2
DB, 0 – 44 μm	Dead-burned CAFB - 9, 1550°C, 24 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1250°C, 2 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1250°C, 5 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1250°C, 24 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1550°C, 2 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1550°C, 5 hr	"	< 0.2
DB, 63 – 88 μm	Dead-burned CAFB - 9, 1550°C, 24 hr	"	< 0.2
Room-Temp. Compacts 4A - 7, 14, 28	Room-temp. processed sorbent/ash mixtures for 7, 14, and 28 days	"	< 0.2
4B - 7, 14, 28	" "	"	< 0.2
4C - 7, 14, 28	" "	"	< 0.2
75 - CF - 22	High-temperature hot-pressed CaS/ash compacts	"	< 0.2
75 - CF - 26	High-temperature hot-pressed $CaSO_4$/ash compacts	"	< 0.2
75 - CF - 30	High-temperature hot-pressed CAFB-sorbent/ash compacts	"	< 0.2
TUGCO Ash	Conventional lignite ash	"	< 0.2
Valley Builder	Commercial aggregate	"	< 0.2
FGD Sludge	Untreated and treated	"	< 0.2
Gypsum	Natural, ground	"	< 0.2
Limestone 1359 500 - 1000 μm		"	< 0.2
Calcined Limestone 1359 500 - 1000 μm		"	> 55
Tymochtee Dolomite 1000 - 1200 μm		"	< 0.2

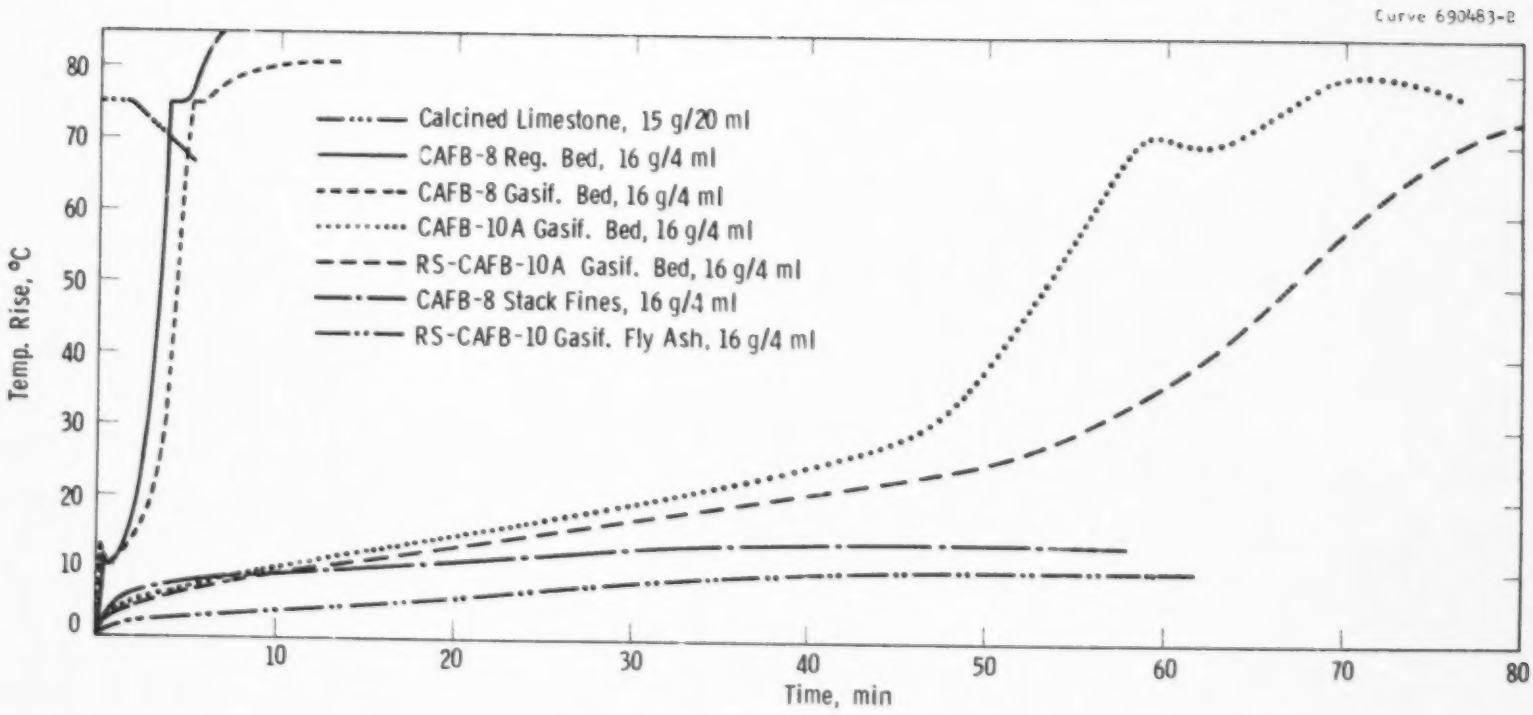

Figure 25 - Heat-Release Property of Spent Solids from the CAFB Process

vary, depending on the soluble components in the particular aqueous system and the temperature of measurement. A constant temperature, 25°C, has been selected for the latter throughout our leaching studies. This section summarizes our efforts in determining empirically the multiplying factor for the CAFB leachates.

Several spent CAFB materials (bed, ash, stack fines) were investigated. Leachate was induced by a 48-hr shake procedure. A portion of the original leachate from each sample was diluted to provide diluted solutions of 1/2, 1/4, and 1/8 fractions of the original concentrations. Specific conductance, pH, and TDS were determined for all 16 leachate solutions.

The procedure in determining TDS described in Standard Method for Water and Wastewater[48] was used to obtain TDS at evaporation temperature, 103°C. This was not the true TDS because the residue at 103°C contained physically occluded water, hydration and carbonation products, $Ca(OH)_2$, $CaSO_4 \cdot 1/2\ H_2O$, $CaSO_4 \cdot 2\ H_2O$, and $CaCO_3$, among other dissolved species. To determine the true TDS - in other words, the total weight of solid from the spent CAFB material that is dissolved - the residue at 103°C was heated to 500°C to convert $Ca(OH)_2$, $CaSO_4 \cdot 1/2\ H_2O$, and $CaSO_4$, and then to 900°C to convert $CaCO_3$ to CaO. As we will show that the TOC in the leachate of CAFB residue is low, volatilization and decomposition of organic species would not be of concern when residue is dried at higher temperatures. The TDS at 900°C was used in this work because it approximated more closely the weight of the actual solid components - for example, CaO and $CaSO_4$ dissolved from the spent CAFB materials.

The results presented in Figure 26 show the relationship between TDS and specific conductance. There is a straight line with a slope of 0.37 mg-cm-$\mu mho^{-1}\ell^{-1}$. Thus, TDS in a CAFB leachate (mg/ℓ) can be approximated by multiplying the easily measured specific conductance (in μmhos/cm) with a conversion factor of 0.37.

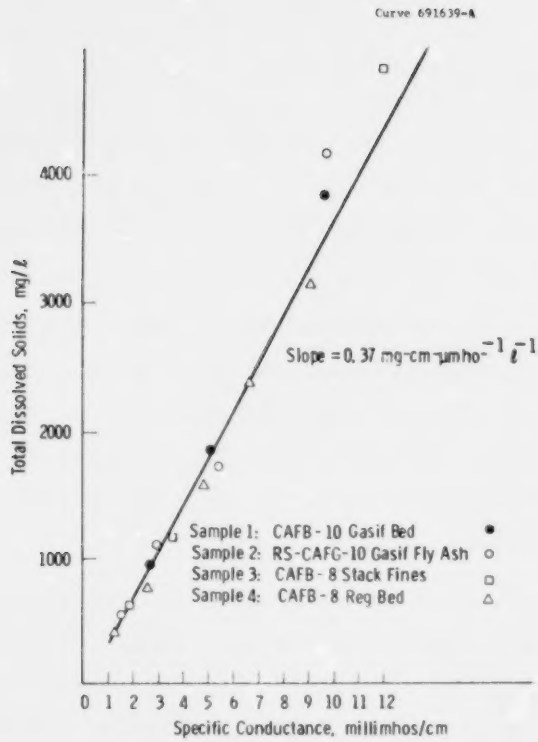
Curve 691639-A
Total Dissolved Solids, mg/ℓ
4000
3000
2000
1000
Slope = 0.37 mg-cm-μmho^{-1} ℓ$^{-1}$
Sample 1: CAFB - 10 Gasif Bed
Sample 2: RS-CAFG-10 Gasif Fly Ash
Sample 3: CAFB - 8 Stack Fines
Sample 4: CAFB - 8 Reg Bed
0 1 2 3 4 5 6 7 8 9 10 11 12
Specific Conductance, millimhos/cm

Figure 26 - Correlation between TDS and Specific Conductance in CAFB Leachate System

Note that the results presented here are empirical and based on typical CAFB leachates. TDS obtained in this manner are only approximated values. Note, also, that a typical CAFB leachate has a TDS of approximately 4000 mg/ℓ and that the drinking water standard for TDS is 500 mg/ℓ.

Total Organic Carbon (TOC)

Conventionally, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are determined on water and waste water streams to provide a measure of the organic content in the stream, but since both the COD and BOD are time-consuming procedures, total organic carbon (TOC) is often measured to provide a speedy and convenient way of estimating the degree of organic contamination.[48]

We used a Model 915 Beckman TOC analyzer. Measurements of TOC on the CAFB residues indicated that the organic content in leachates of CAFB residue was insignificant when compared with gypsum leachate as a control.

Leaching Media

In the previous sections deionized water was based in the majority of the leaching tests except where otherwise specified. Leaching property of the CAFB residue was also investigated as a function of leaching media. Three media of varying pH were used. Leaching with CO_2-saturated deionized water was carried out to simulate surface water where dissolved CO_2 may be high. Leaching tests were also conducted using a sodium acetate/acetic acid buffer solution with a pH = 4.4 and specific conductance 3.31 μmhos/cm, as suggested by the proposed ASTM test[32] to simulate inhomogeneous disposal sites where codisposal of municipal and industrial waste often results in acidic leaching conditions. Table 34 summarizes the continuous leaching results of CAFB-10A gasifier bed material using three media under aerobic and anaerobic conditions. Definitive conclusions cannot be drawn on the basis of such limited data, but preliminary results do indicate the following:

- Specific conductance and pH were decreased slightly with CO_2-saturated media because of the formation of insoluble $CaCO_3$.
- The effect of an acetate medium on leachate concentrations was more than additive, perhaps due to the higher ionic strength and lower pH of the leaching medium. Increased calcium and sulfide in the acetate leachate were such examples.
- Anaerobic leachate had higher sulfide in all cases.
- On the whole the leaching medium did not play as important a role as one might have expected, due to the large amount of spent CaO present in the CAFB residue.
- The final leachates were still highly alkaline in all cases (pH ~12).

Minor and trace species were determined in these leachates. Preliminary results, based on single-test data, suggested a slight

Table 34

CHEMICAL CHARACTERISTICS OF CAFB-10A LEACHATE USING DIFFERENT ELUENT

Eluent	Eluent pH	Solid / Eluent Ratio	Continuous Shake Time hr	Aerobic / Anaerobic	Leachate Chem. Characteristics				
					pH	Sp. Conductance (millimhos/cm)	Ca, mg/ℓ	$S^{=}$, mg/ℓ	SO_4, mg/ℓ
Deionized Water	7.0	1:10	100	Aerobic	12.2	11.13	1708	-	1263
Deionized Water	7.0	1:10	100	Anaerobic	12.2	11.23	1768	150	1311
Deionized Water	7.0	1:10	196	Aerobic	12.3	11.74	1572	91	1395
Deionized Water	7.0	1:10	196	Anaerobic	12.3	8.62	1472	374	1139
CO_2-Saturated Deionized H_2O	4.0	1:10	200	Aerobic	11.9	9.59	1520	255	1225
CO_2-Saturated Deionized H_2O	4.0	1:10	200	Anaerobic	11.9	9.57	1568	369	1083
CO_2-Saturated Deionized H_2O	4.0	1:10	400	Aerobic	12.0	9.73	1600	344	1460
CO_2-Saturated Deionized H_2O	4.0	1:10	400	Anaerobic	12.0	9.70	1572	552	1325
Acetate Buffer SC = 3.1 millimhos/cm	4.4	1:10	200	Aerobic	12.1	14.5	3276	329	913
Acetate Buffer SC = 3.1 millimhos/cm	4.4	1:10	200	Anaerobic	12.0	14.9	3280	397	1248
Acetate Buffer SC = 3.1 millimhos/cm	4.4	1:10	400	Aerobic	12.2	14.8	3400	363	1060
Acetate Buffer SC = 3.1 millimhos/cm	4.4	1:10	400	Anaerobic	12.1	19.2	4830	656	840

increase in lead, selenium, mercury, and chlorine. Because of sample inhomogeneity and variations among CAFB residues from different run conditions, tests on more samples must be repeated.

SUMMARY

The leachate characteristics of unprocessed and processed CAFB spent sorbent are summarized in Figure 27 and compared with natural gypsum leachate. Note the improvement of leachate quality by various processing alternatives. This investigation, in general, resulted in the following findings:

- Trace elements are not expected to cause environmental problems (unprocessed and processed).
- Negligible organic contamination was found in the leachate (unprocessed and processed).
- Leaching and heat release are improved significantly by processing the stone.
- The leachate quality of processed spent sorbent has been shown to be equal to or better than natural gypsum leachate.
- Potential concerns are for

  Unprocessed: sulfide, heat-release, Ca, SO_4, TDS, and pH

  Processed: Ca, SO_4, TDS, and pH.

The effect of the leaching medium on leaching property should be investigated further. Although TOC is low in leachates, specific organic species have not been determined.

Because we lack specific disposal criteria, the leachate characteristics of the CAFB residue are compared with liquor and leachate of FGD residue, a currently commercialized process (Table 35). The untreated sludge has liquor and leachate exceeding many of the DWS for trace elements. With very few exceptions (two batches of stack fines), the leachate of the CAFB residues meet the stringent DWS.

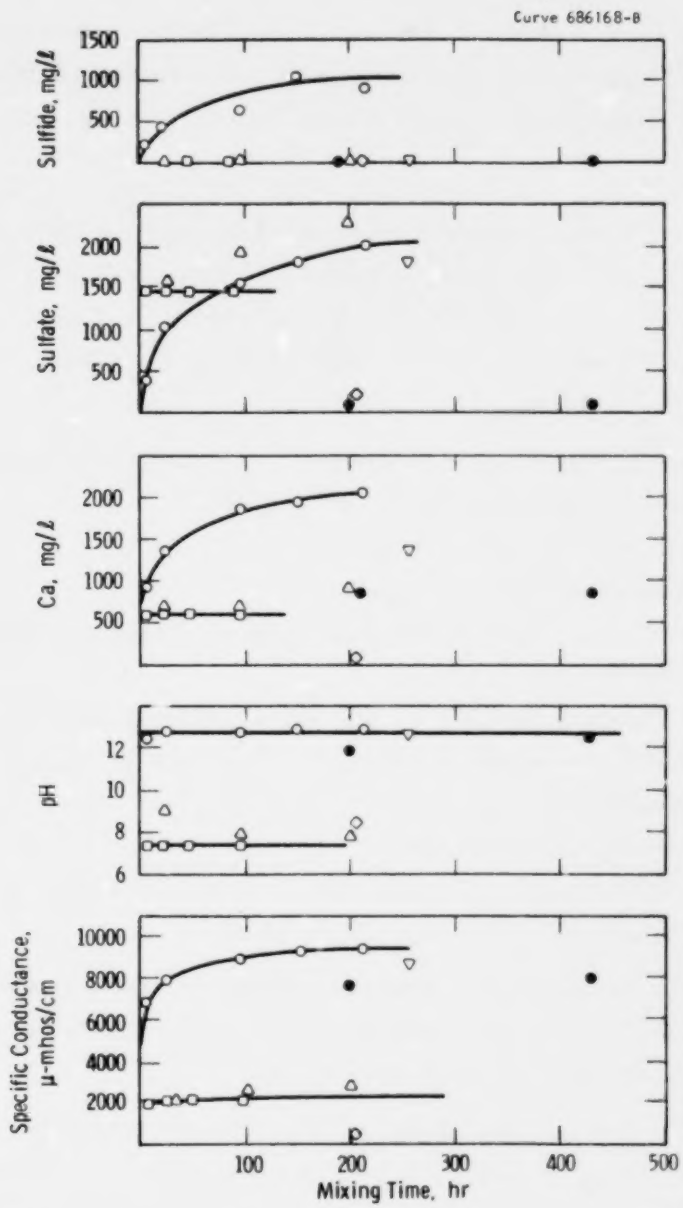

Figure 27 - Leachate Characteristics as a Function of Mixing Time for:

- ○ CAFB-9, unprocessed
- △ CAFB-904, 94 m% dry-sulfated
- ● Dead-burned at 1550°C, 5 hr
- ▽ Room-temp. processed compacts
- ◇ 75-CF-30, hi-temp. processed compact
- □ Natural gypsum

Table 35

Dwg. 1693B72

COMPARISON OF LEACHATE CHARACTERISTICS FROM THE CAFB AND FGD RESIDUES*

Substance	Liquor, mg/ℓ	Leachate, mg/ℓ		Drinking Water Standards,** mg/ℓ
	FGD	CAFB	FGD	
Al	0 to 20	< 1	< 1	
Ag	< 0.05	< 0.05	< 0.05	0.05
As	< 0.05	< 0.05	0 to 0.1	0.05
B	> 5	< 2	> 1	
Ba	< 1	< 1.0	< 1	1.0
Be	< 0.02	< 0.02	< 0.02	
Bi	< 0.04	< 0.04	< 0.04	
Ca	> 500	> 500	> 500	200
Cd	0 to 0.2	< 0.01	< 0.01	0.01
Co	< 0.1	< 0.1	< 0.1	
Cr	< 0.05	< 0.05	< 0.05	0.05
Cu	< 1	< 0.1	< 0.1	1.0
Fe	< 0.3	a < 0.3 to > 1	< 0.3	0.3
Hg	< 0.002	a < 0.03	< 0.002	0.002
Mg	0 to > 1000	< 20	0 to 500	75
Mn	0 to 20	< 0.05	0 to 0.1	0.05
Mo	0.1 to 7.0	< 1	< 1	
Na	0 to > 100	< 10	< 10	
Ni	< 1	< 0.1	< 0.1	2.0
Pb	< 0.05	< 0.05	< 0.05	0.05
Sb	< 0.2	< 0.1	< 0.1	
Se	0.001 to 0.5	a < 0.01 to 0.15	0 to 0.1	0.01
Si	0 to 30	< 2	0 to 5	
Sn	< 1.0	< 1.0	< 1.0	1.0
Sr	0 to 40	0 to > 10	0 to 5	
Ti	< 2	< 2	< 2	
V	< 2	< 1	< 1	
Zn	< 2	< 1	< 1	5.0
Zr	< 2	< 1	< 1	
S=	< 20	0 to > 1000	< 20	
SO_3	< 10 to 40	< 10	< 10	
SO_4	1000 to 7000	1000-2000	1000-2000	250
Cl	300 to 6000	< 30	30 to 300	250
F	10 to 50	a < 2.4 to 8	1 to 10	2.4
NO_3(as N)	0 to 100	< 10	< 10	10
TOC	< 30	< 30	< 30	
pH	6 to 9	12 to 13	6 to 9	5 to 9
TDS	5000 to 14000	3000 to 4000	2000 to 3000	500
Specific Conductance μmhos/cm	5.0 to 17.0	6.0 to 10.0	2.0 to 3.0	

* Untreated

** NIPDWR and USPHS (1962) Drinking Water Standards, and WHO Potable Water Standards

a DWS Exceeded by ≤ 2 Carry-over Samples

▨ Exceed Drinking Water Standards

4. ENVIRONMENTAL ASSESSMENT

Based on the laboratory testing results, we judged that the unprocessed CAFB spent sorbent would not be environmentally acceptable for direct land disposal. Available test data, however, show that environmental acceptability can be achieved by further processing. Table 36 summarizes the degree of reduction of the environmental impact achieved by four of the processing alternatives for the spent sorbent from the CAFB gasification process. The leaching tests performed are considered to result in more severe projections of environmental impact than will be encountered in practice. Since there are no guidelines for leachate qualities at the present time, results are compared with drinking water standards and leachate characteristics of natural gypsum.

It must be pointed out that the drinking water standards are used in this investigation only in an effort to put data into perspective in the absence of EPA guidelines and should not be construed as suggesting that the leachate must necessarily meet drinking water standards. Of course, these standards are extremely conservative; a leachate dilution/attenuation factor of 10 is currently being considered in the regulation draft under Section 3001 of the RCRA by the Hazardous Waste Management Division of the Office of Solid Waste, EPA.[17]

Although, on the basis of its leachate quality (Table 36), the high-temperature processed compact appears to be environmentally superior to other alternatives, the energy requirements would have to be evaluated in relation to the benefits. On the basis of environmental impact, dry-sulfation would be the recommended process, followed by dead-burning and low-temperature fly ash blending.

Dwg. 1694B48

Table 36

COMPARISON OF ENVIRONMENTAL IMPACT OF PROCESSED AND UNPROCESSED CAFB SPENT SORBENTS

Environmental Parameters / Processing	pH	Total Dissolved Solids	Sulfide[a]	Sulfate	Calcium	Trace Metal	Heat Release 3g/20 ml[a]	Total Organic Carbon[a]
Unprocessed CAFB	u	u	u	u	u	u	ΔT = 18°C	u
Dry-Sulfation	+	+	+	0	+	0	ΔT = ND < 0.2°C	0
Dead-Burning	0	0	+	+	+	0	ΔT = ND < 0.2°C	0
Rm-temp. Processing	0	0	+	0	+	0	ΔT = ND < 0.2°C	0
Hi-temp. Processing	+	+	+	+	+	0	ΔT = ND < 0.2°C	0

Note: u Unprocessed CAFB leachate characteristics
+ Improved from u value
0 No significant change from u value

Do not meet either the drinking water or gypsum leachate criteria

Pass gypsum leachate criteria but not Drinking Water Standards

Pass both drinking water and gypsum leachate criteria

a No Drinking Water Standards exist

The major environmental concerns for direct disposal are heat release, sulfide, pH, calcium, SO_4, and TDS. The major environmental conerns for disposal after processing are pH, calcium, SO_4, and TDS. On the basis of these results, spent sorbent processing will be required. There are advantages and disadvantages to each method of processing, but the ultimate decision will be based on the careful balance of technical achievement and economic feasibility. Of course, site selection, design, and management of the disposal task based on the site-specific hydrology, geology, climate, and soil composition are critically important to the success of a solid waste disposal system. Selection of a proper processing method to reduce the residue surface area and permeability and to improve the heat-release and leaching properties can greatly simplify the disposal management task.

In the absence of formal EPA criteria with which to assess the environmental acceptability of the disposal of CAFB residues, the chemical, physical, and leaching properties of the spent fluidized-bed combustion (FBC) material are compared with those of the residues from six FGD processes developed for conventional coal-burning power plants. A preliminary comparison of the environmental impact of the disposal of unprocessed CAFB solid wastes and untreated FGD sludge residues from varying processing systems is presented in Table 36 on the basis of up-to-date results from parallel environmental testing programs. Since the samples tested resulted from our use of different coal and sorbents, an absolute comparison may not be possible, although one would hope that the general trends indicated were meaningful.

These results are encouraging and suggest that the disposal of the CAFB solid waste may cause environmental effects comparable to (due to its chemical properties) or perhaps less negative than (due to its physical properties) the disposal of the residue from the currently commercialized FGD process.

The assessment is based on the current results from an ongoing program that is limited, however, by the lack of spent CAFB materials from commercial systems. These conclusions are considered preliminary and should be reassessed as more representative samples become available.

Table 37

Dwg. 2515C80

PRELIMINARY COMPARISON OF THE ENVIRONMENTAL IMPACT OF THE DISPOSAL OF CAFB AND FGD RESIDUES*

	CAFB	FGD
Chemical Property	① Solubility of major compounds: Ca, SO_4, and TDS contributing to potential environmental concern	① High concentrations of Mg, Cl in addition to Ca, SO_4 and TDS (plus Na in the case of double-alkali system)
	② Sulfide: environmental concern	② Sulfite: environmental concern
	③ High alkalinity in leachate: pH = 10 to 13	③ pH = 5 to 10 for lime or limestone scrubbing systems pH = 12 to 13 for double-alkali system
	④ Trace elements: not expected to cause environmental problem. Most leachates meet Drinking Water Standards	④ Several elements in liquor and leachate, e.g. As, Se, Cd, Mn and F, exceeding the Drinking Water Standards including the ponded and oxidized sludges
	⑤ TOC in leachate: low	⑤ TOC in leachate: low TOC in liquors: low
Physical Property	① Residual activity : Heat - release due to hydration of CaO	① No heat - release problem
	② Spent sorbent in dry granular solid form • More disposal and utilization options available • Relative ease in transporting and disposal	② In sludge form • Difficulty in dewatering and settling of untreated sludge causing problems in land disposal • Potential environmental problems associated with transporting, ponding, and land reclamation
	③ Further processing is recommended due to presence of CaS and CaO	③ Physical stabilization chemical fixation or oxidation to high solids content gypsum most likely required

*Unprocessed CAFB residue and untreated FGD sludge

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